

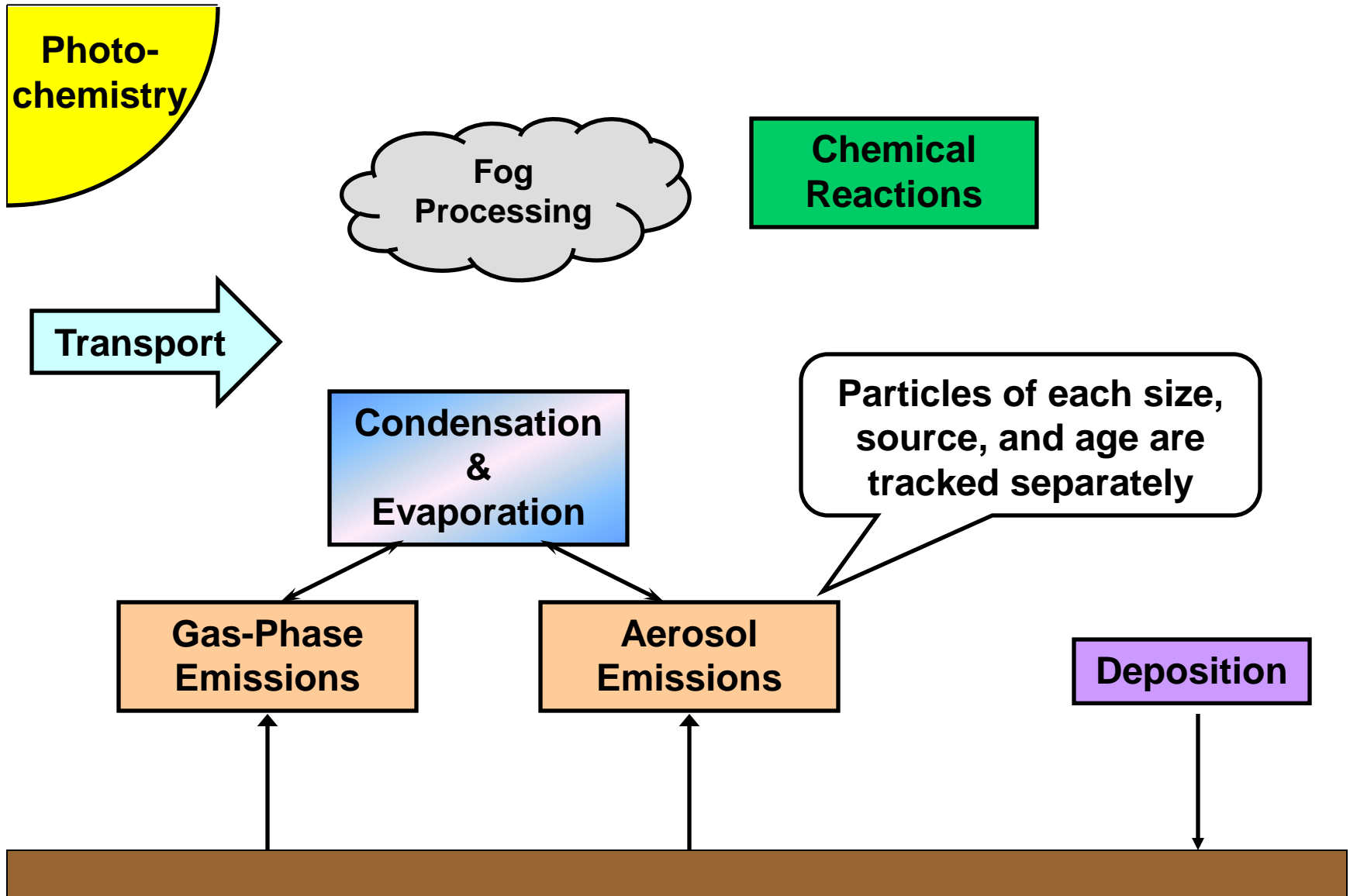
Fine Particulate Matter in the San Joaquin Valley: Review of Modeling Results From CRPAQS

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Mechanistic Air Quality Models



Chemical Mechanism

LIST OF REACTIONS AND RATE

THERMAL RATE CONSTNA
PHOTOLYSIS RATE CONS
ARRHENIUS RATE EXPRE
(TEMP/TREF)**B, WHERE TREF

NO. LBL K (A EA B) REACTION

1 1 5.331E-01 PHOT=NO2 NO2 + HV = NO + O3P

2 2 2.102E-05 (2.040E-05 0.00 -4.800) O3P + O2 + M = O3 + M

3 3

4 4

5 5

6 6

7 7

8 8

9 9

10 11 7.098E-10 (1.185E-10 -1.05 -2.000) NO + NO + O2 = #2 NO2

11 12 2.268E+03 (1.006E-01 0.00 -5.500)

12 12

13 13

14 14

15 15

16 16

17 20 2.959E-02 PHOT=O3O3P O3 + HV = O3P + O2

18 21 2.612E-03 PHOT=O3O1D O3 + HV = O*1D2 + O2

19 22 3.249E+05 (3.229E+05 0.00 -1.000) O*1D2 + H2O = #2 HO.

20 20

21 21

22 22

23 23

24 24

25 25

26 29 2.955E+04 (2.936E+04 0.00 -1.000) HO. + NO2 = HNO3

27 30 1.549E+02 (9.468E+00 -1.65 -1.000) HO. + HNO3 = H2O + NO3

28 31 4.640E-05 PHOT=HNO3 HNO3 + HV = HO. + NO2

29 29

30 30

31 31

32 32

33 33

34 37 4.028E-04 PHOT=HO2NO2 HNO4 + HV = #.61 HO2. + #.61

NO2 + #.39 HO. + #.39 NO3

35 38 7.408E+03 (2.202E+03 -0.71 -1.000) HNO4 + HO. = H2O + NO2 + O2

36 39 2.765E+00 (2.055E+01 1.19 -1.000) HO2. + O3 = HO. + #2 O2

37 40A 2.591E+03 (3.229E+02 -1.23 -1.000) HO2. + HO2. = HO2H + O2

38 40B 1.436E-01 (1.113E-05 -5.60 -2.000) HO2. + HO2. + H2O = HO2H + O2 +

H2O

39 41 5.909E+03 (5.872E+03 0.00 -1.000) NO3 + HO2. = #.8 HO. + #.8 NO2

+ #.8 O2 + #.2 HNO3 + #

40 40

41 41

42 42

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49 49

50 50

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52 52

53 53

54 54

55 55

56 56

57 57

58 58

59 59

60 60

46 MER1 1.075E-04 (4.110E+03 -0.57 -1.000) C-O2. + NO = NO2 + HCHO + HO2.

47 MER4 7.682E+03 (5.578E+02 -1.55 -1.000) C-O2. + HO2. = COOH + O2

48 MEN3 1.920E+03 (1.908E+03 0.00 -1.000) C-O2. + NO3 = HCHO + HO2. + NO2

49 MFR5 3.910E+02 (3.596E+01 -1.41 -1.000) C-O2. + C-O2. = MECH + HCHO +

1.582E+02 (8.661E+02 1.01 -1.000) C-O2. + C-O2. = #2 HCHO + #2

1.333E+04 (3.963E+03 -0.71 -1.000) RO2-R. + NO = NO2 + HO2.

2.196E+04 (2.789E+02 -2.58 -1.000) RO2-R. + HO2. = ROOH + O2 + #3

3.397E+03 (3.376E+03 0.00 -1.000) RO2-R. + NO3 = NO2 + O2 + HO2.

2.955E+02 (2.936E+02 0.00 -1.000) RO2-R. + C-O2. = HO2. + #.75

MECH

55 RRR2 5.170E+01 (5.138E+01 0.00 -1.000) RO2-R. + RO2-R. = HO2.

56 R2NO 1.333E+04 K SAME AS RXN R2NO

R2O2. + NO = NO2

R2O2. + HO2. = HO2.

R2O2. + NO3 = NO2

R2O2. + C-O2. = C-O2.

R2O2. + RO2-R. = RO2-R.

R2O2. + R2O2. =

RO2-N. + NO = RNO3

RO2-N. + HO2. = ROOH + #3 XC

RO2-N. + C-O2. = HO2. + #.25

#.5 PROD2 + #.75 HCHO + XC

RO2-N. + NO3 = NO2 + O2 +

RRR2 RO2-N. + RO2-R. = HO2. +

XC

RRR2 RO2-N. + R2O2. = RO2-N.

RRR2 RO2-N. + RO2-N. = MEK + HO2.

-9.100)

1.900)

.000

CCO-O2. + NO2 = PAN

A(2.400E+18 27.03 0.000)

F = 0.300 N = 1.000

PAN = CCO-O2. + NO2

CCO-O2. + NO = C-O2. + CO2 +

-1.000) CCO-O2. + HO2. = #.75 CCO-OH +

#.25 CCO-OH + #.25 O3

-1.000) CCO-O2. + NO3 = C-O2. + CO2 +

-1.000) CCO-O2. + C-O2. = CCO-OH + HCHO

-1.000) CCO-O2. + RO2-R. = CCO-OH

CCO-O2. + R2O2. = CCO-O2.

CCO-O2. + RO2-N. = CCO-OH +

2.294E+04 (4.257E+03 -0.99 -1.000) CCO-O2. + CCO-O2. = #2 C-O2. +

#2 CO2 + O2

79 FPN2 1.782E+04 (1.761E+04 0.00 -1.900) RCO-O2. + NO2 = PAN2

80 PAN2 2.689E-02 (1.200E+17 25.44 0.000) PAN2 = RCO-O2. + NO2

81 FPN0 4.131E+04 (1.835E+04 -0.48 -1.000) RCO-O2. + NO = NO2 + CCHO +

RO2-R. + CO2

2 = #2 NO2 + O2

V = #2 HO.

O. = HO2. + H2O

2. = H2O + O2

= HO2. + SULF

= HO2. + H2O

C-O2. + NO = NO2 + HCHO + HO2.

C-O2. + HO2. = COOH + O2

C-O2. + NO3 = HCHO + HO2. + NO2

C-O2. + C-O2. = MECH + HCHO +

C-O2. + C-O2. = #2 HCHO + #2

RO2-R. + NO = NO2 + HO2.

RO2-R. + HO2. = ROOH + O2 + #3

RO2-R. + NO3 = NO2 + O2 + HO2.

RO2-R. + C-O2. = HO2. + #.75

RO2-R. + RO2-R. = HO2.

R2O2. + NO = NO2

R2O2. + HO2. = HO2.

R2O2. + NO3 = NO2

R2O2. + C-O2. = C-O2.

R2O2. + RO2-R. = RO2-R.

R2O2. + R2O2. =

RO2-N. + NO = RNO3

RO2-N. + HO2. = ROOH + #3 XC

RO2-N. + C-O2. = HO2. + #.25

#.5 PROD2 + #.75 HCHO + XC

RO2-N. + NO3 = NO2 + O2 +

RO2-N. + RO2-R. = HO2. +

RO2-N. + R2O2. = RO2-N.

RO2-N. + RO2-N. = MEK + HO2.

CCO-O2. + NO2 = PAN

CCO-O2. + NO = C-O2. + CO2 +

CCO-O2. + HO2. = #.75 CCO-OH +

CCO-O2. + NO3 = C-O2. + CO2 +

CCO-O2. + C-O2. = CCO-OH + HCHO

CCO-O2. + RO2-R. = CCO-OH

CCO-O2. + R2O2. = CCO-O2.

CCO-O2. + RO2-N. = CCO-OH +

CCO-O2. + CCO-O2. = #2 C-O2. +

CCO-O2. + NO2 = PAN2

PAN2 = RCO-O2. + NO2

RCO-O2. + NO = NO2 + CCHO +

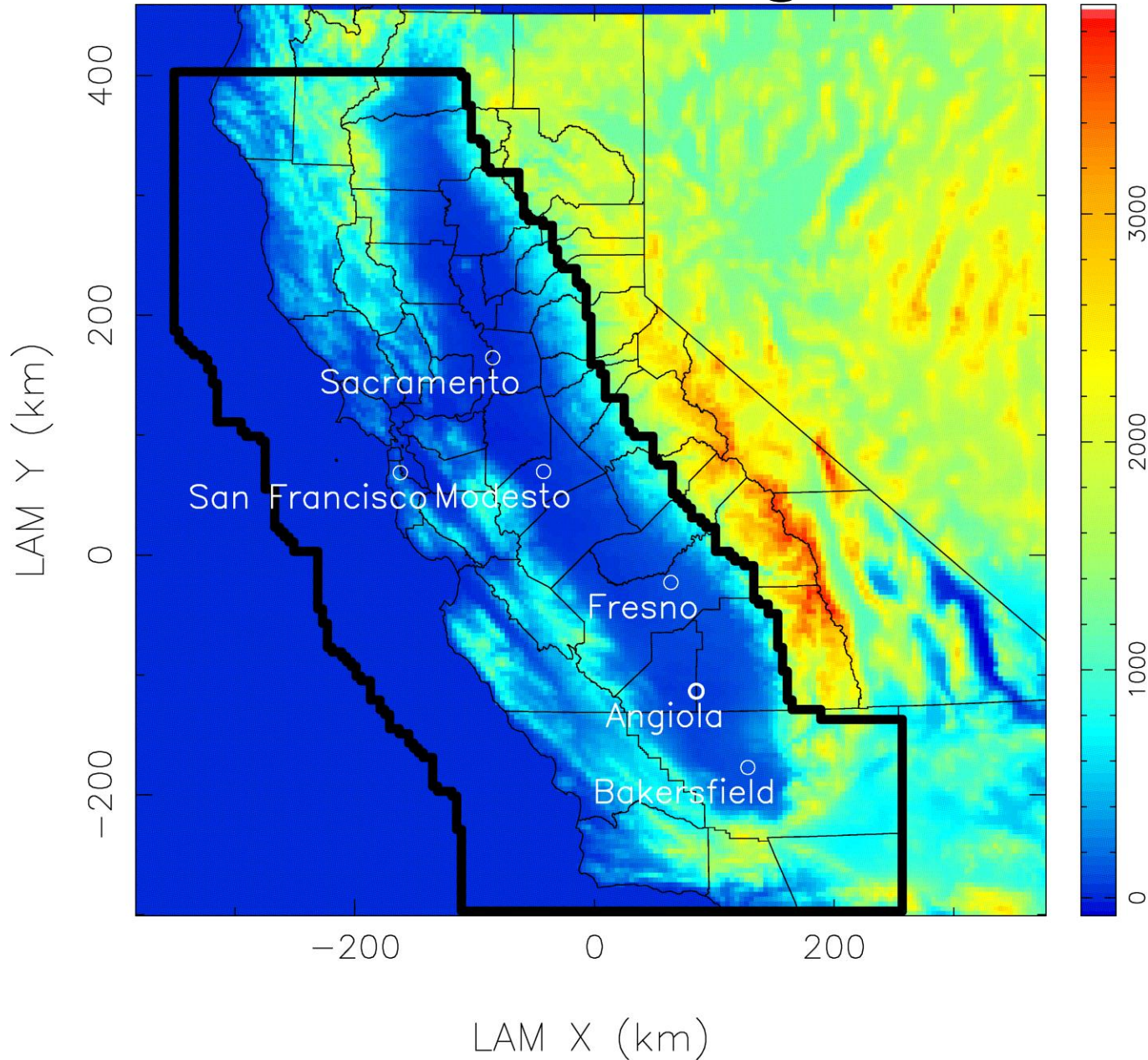
335 Active Species

15 Steady State Radicals

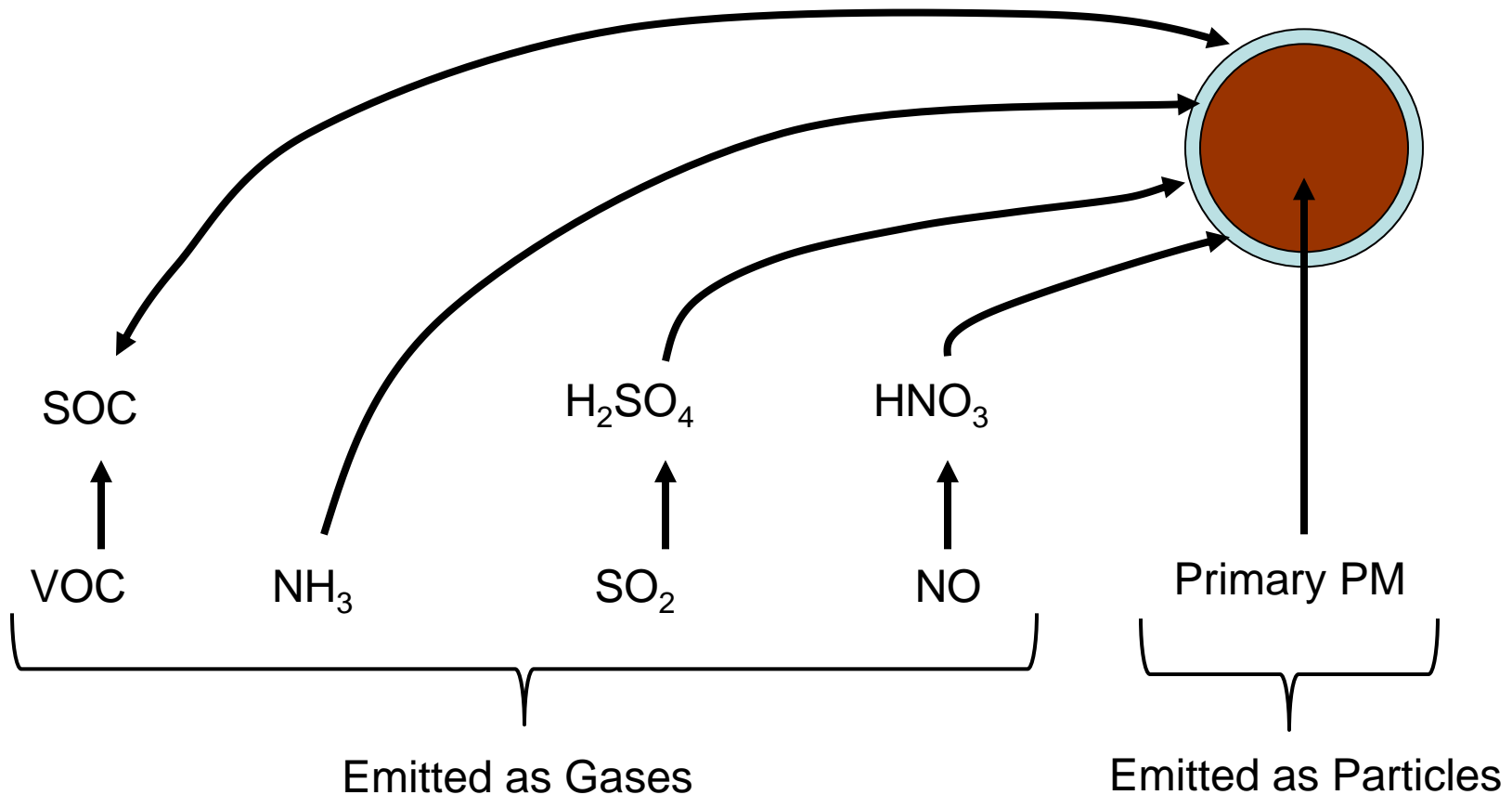
1500 Chemical Reactions

+300,000 grid cells

CRPAQS Modeling Domain



Basic Particle Chemistry



VOC = Volatile Organic Compounds (benzene, ethanol, formaldehyde, ...)

SOC = semi-volatile organic compounds (mostly unknown)

Primary PM = particulate matter emitted directly from sources (trace metals – aluminum, silicon, iron, nickel, etc, elemental carbon, organic carbon)

CRPAQS PM2.5 Mass

Black Line – measurements

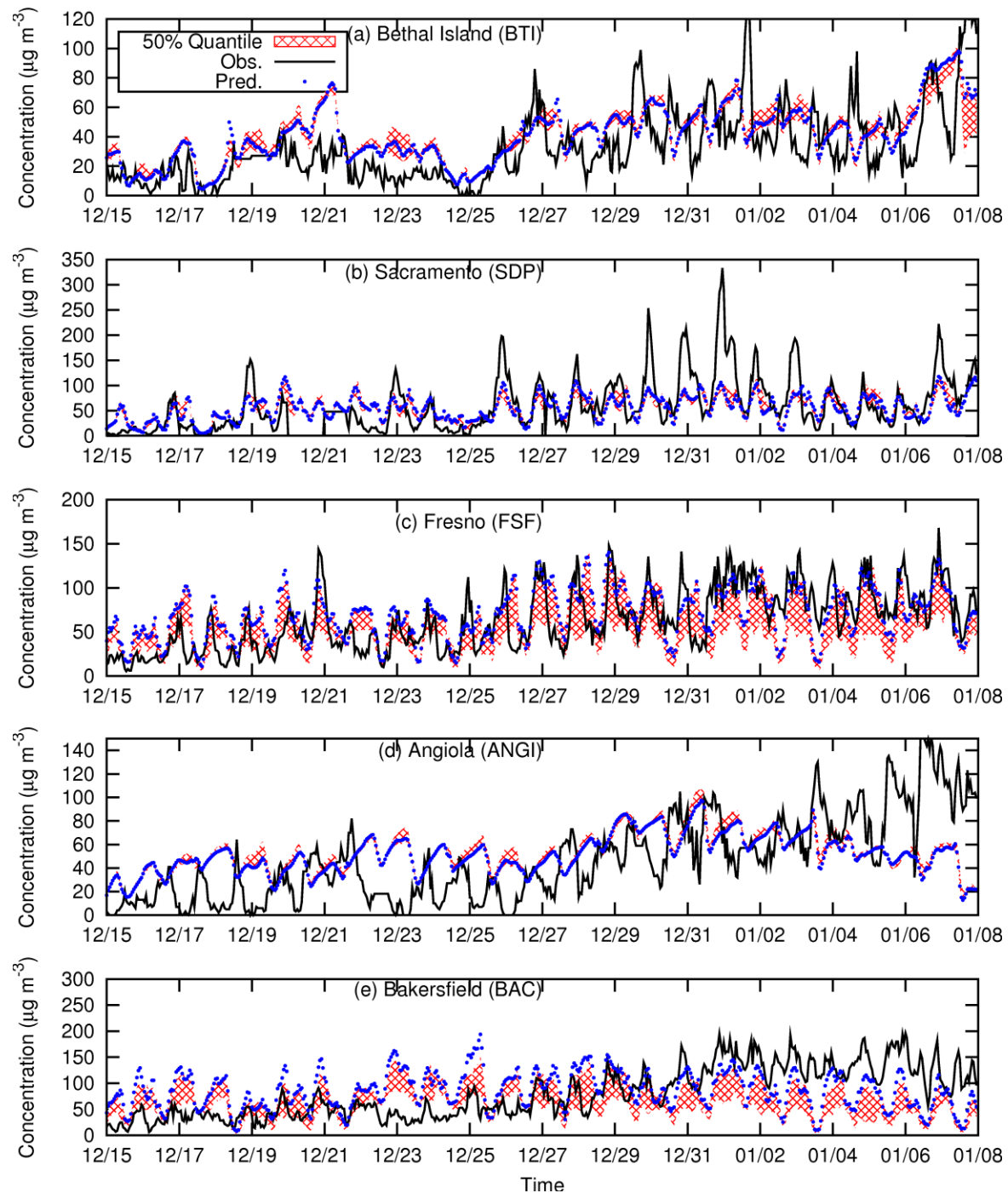
Blue Line – predictions

Red Shading – Mid 50%
Quantile within 10km of
monitor

Major trends are captured at
most stations

Under-prediction of mass at
Angiolo and Bakersfield near
the end of the episode

Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., 42, pg8954-8966, 2008.



Relative Component Contributions to PM

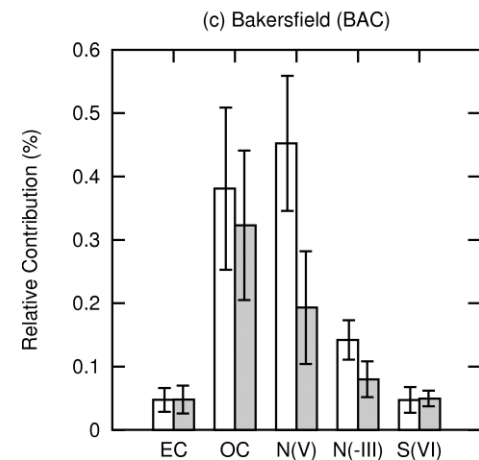
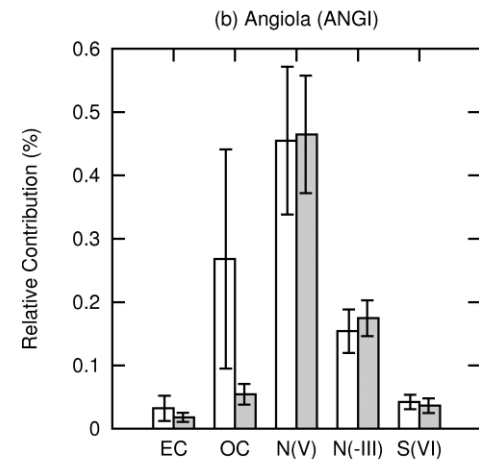
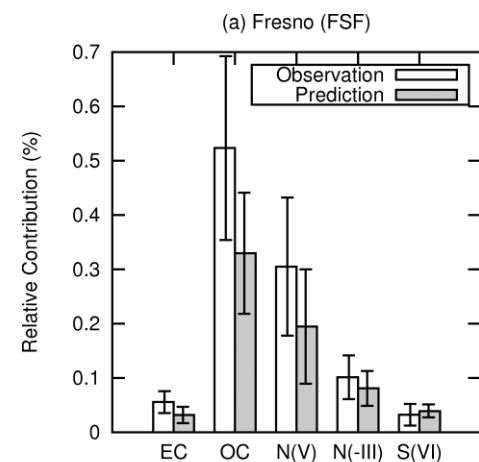
Average and standard deviation of predictions and observations is based on 55 samples

Urban locations (Fresno and Bakersfield)

Predictions and observations match except for nitrate under-prediction at Bakersfield

Rural location (Angiola)

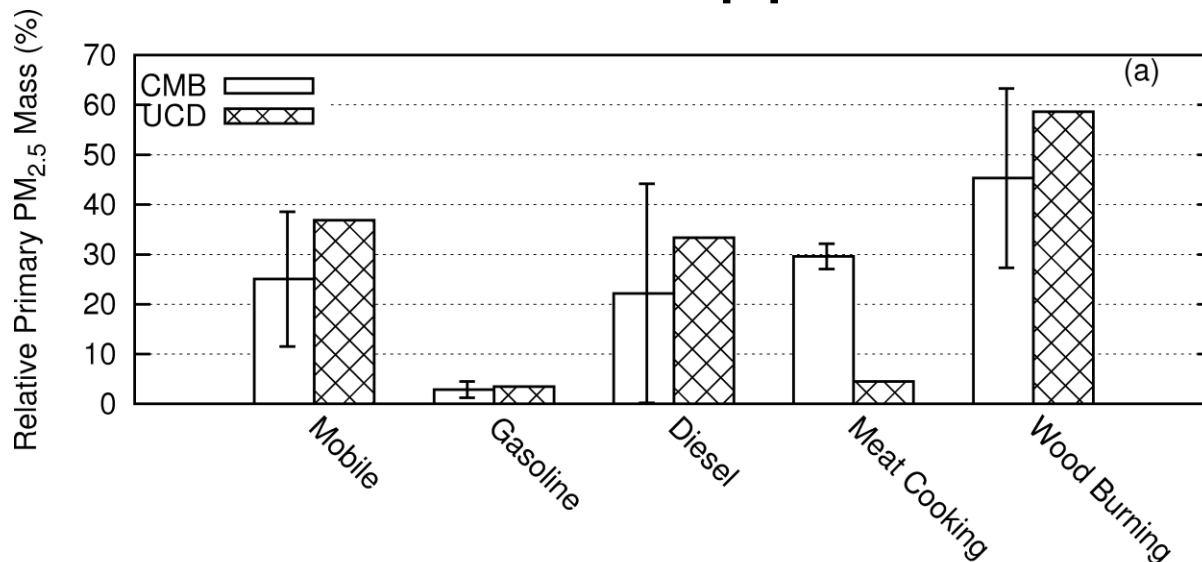
OC under-prediction. What primary sources are we missing? What SOA formation mechanisms are we missing?



Grid Model vs. CMB Source Apportionment

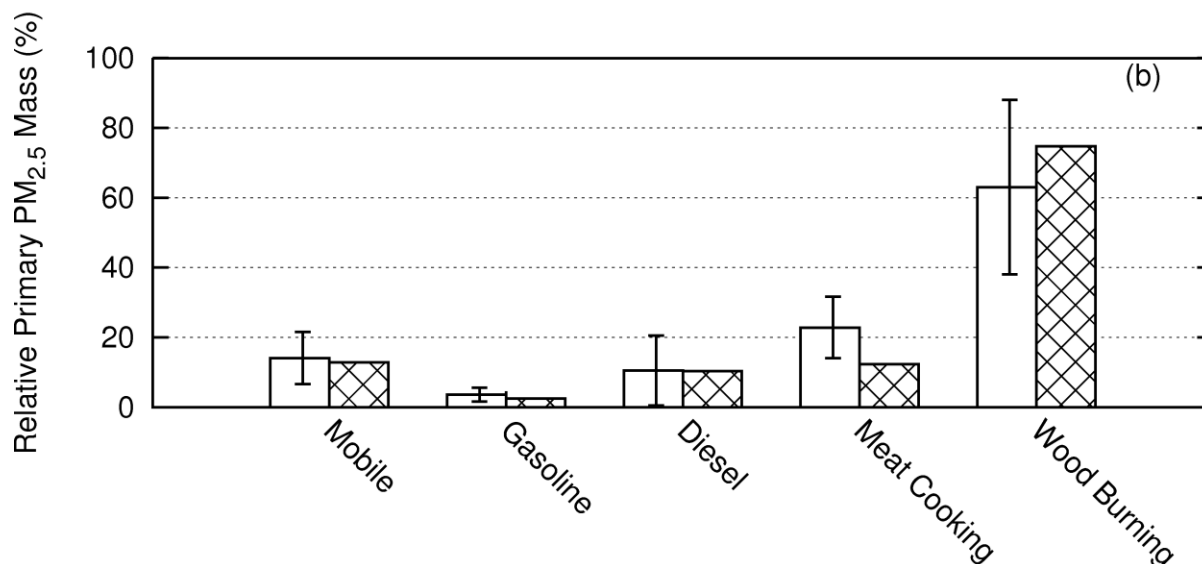
Angiola

**Dust sources removed from grid model



Fresno

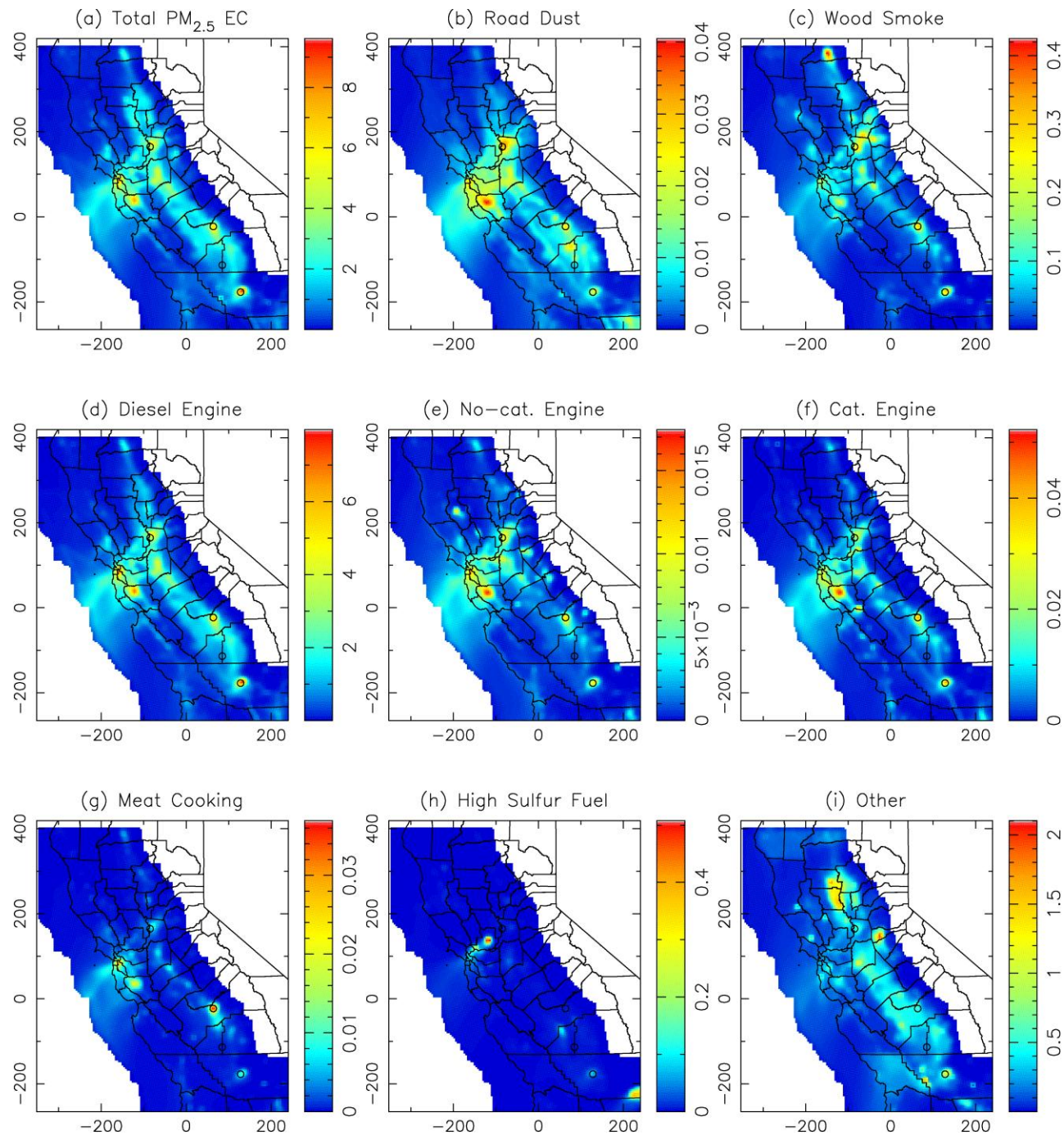
**Dust sources removed from grid model



Regional EC Source Contributions

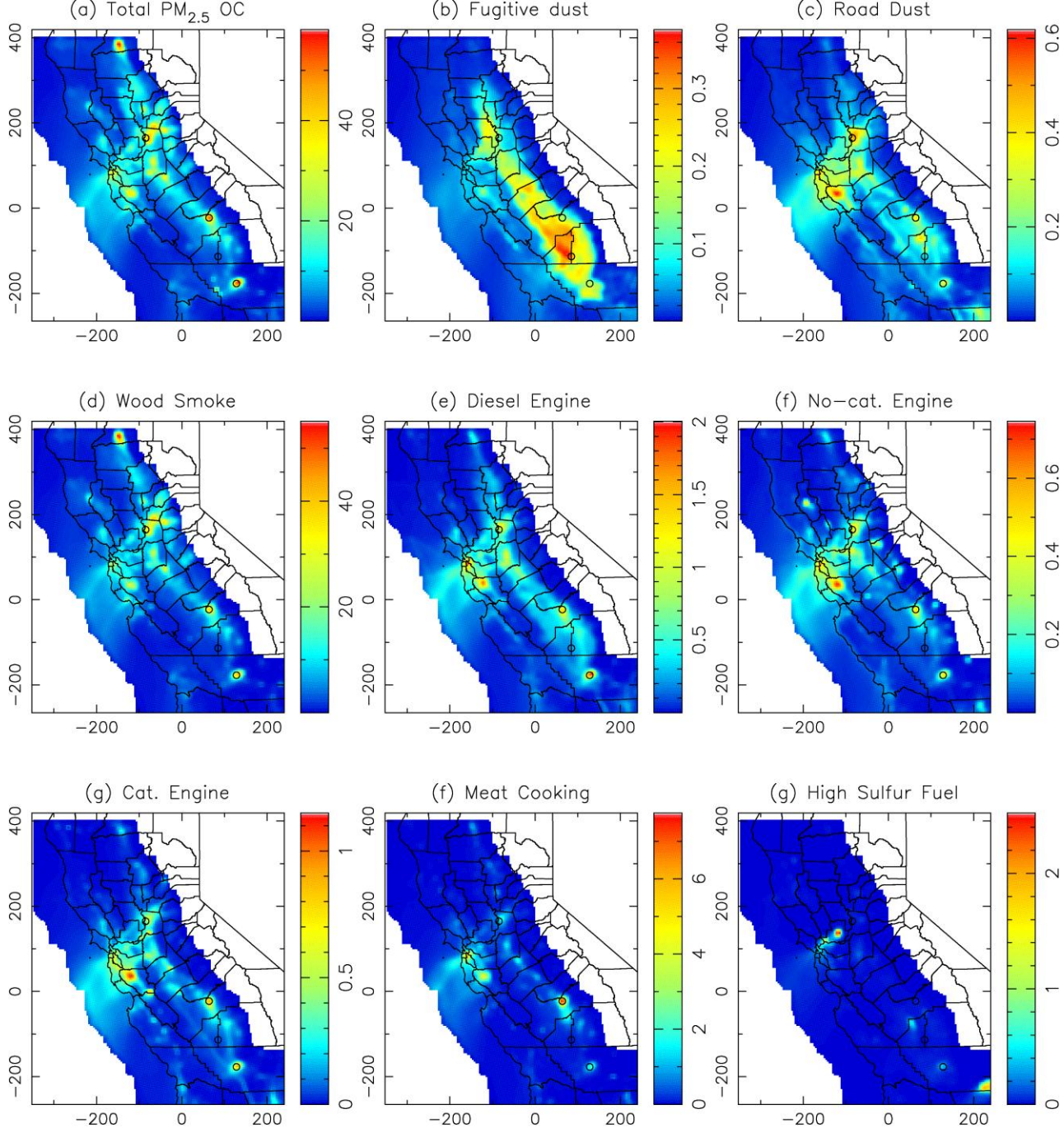
Urban hotspots

Diesel dominates



Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part II. Regional Source Apportionment of Primary Airborne Particulate Matter.", Atmos. Env., 42, pp8967-8978, 2008.

Regional OC Source Contributions



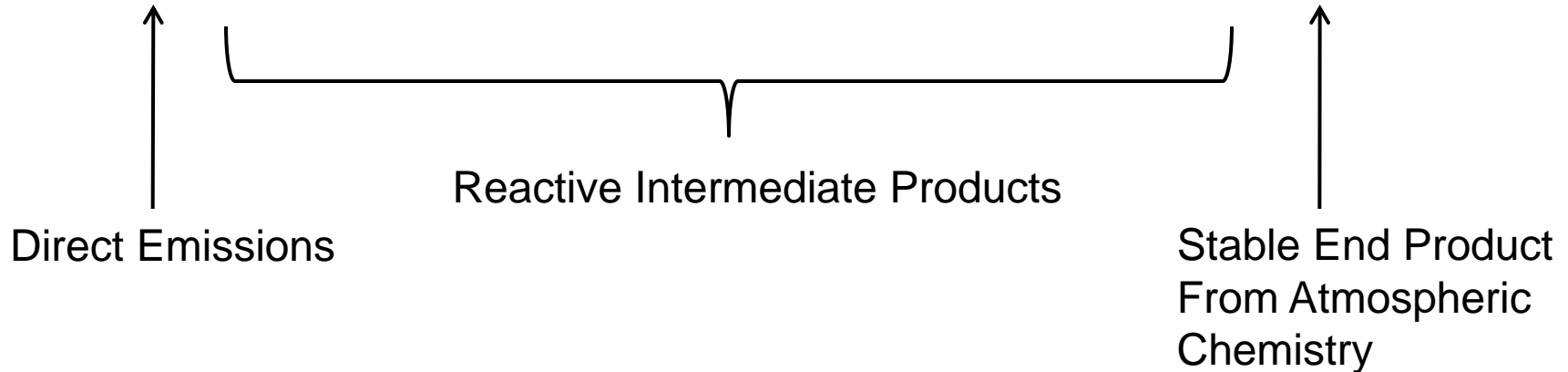
Urban hotspots

Wood smoke dominates

Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part II. Regional Source Apportionment of Primary Airborne Particulate Matter.", *Atmos. Env.*, 42, pp8967-8978, 2008.

Spectrum of Reactive Nitrogen Compounds

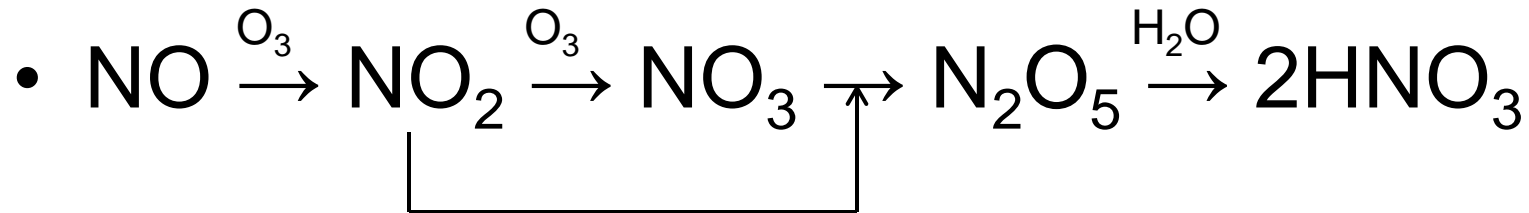
- NO, NO₂, NO₃, N₂O₅, HONO, PAN, HNO₃



Direct Emissions

Particle Phase Nitrate

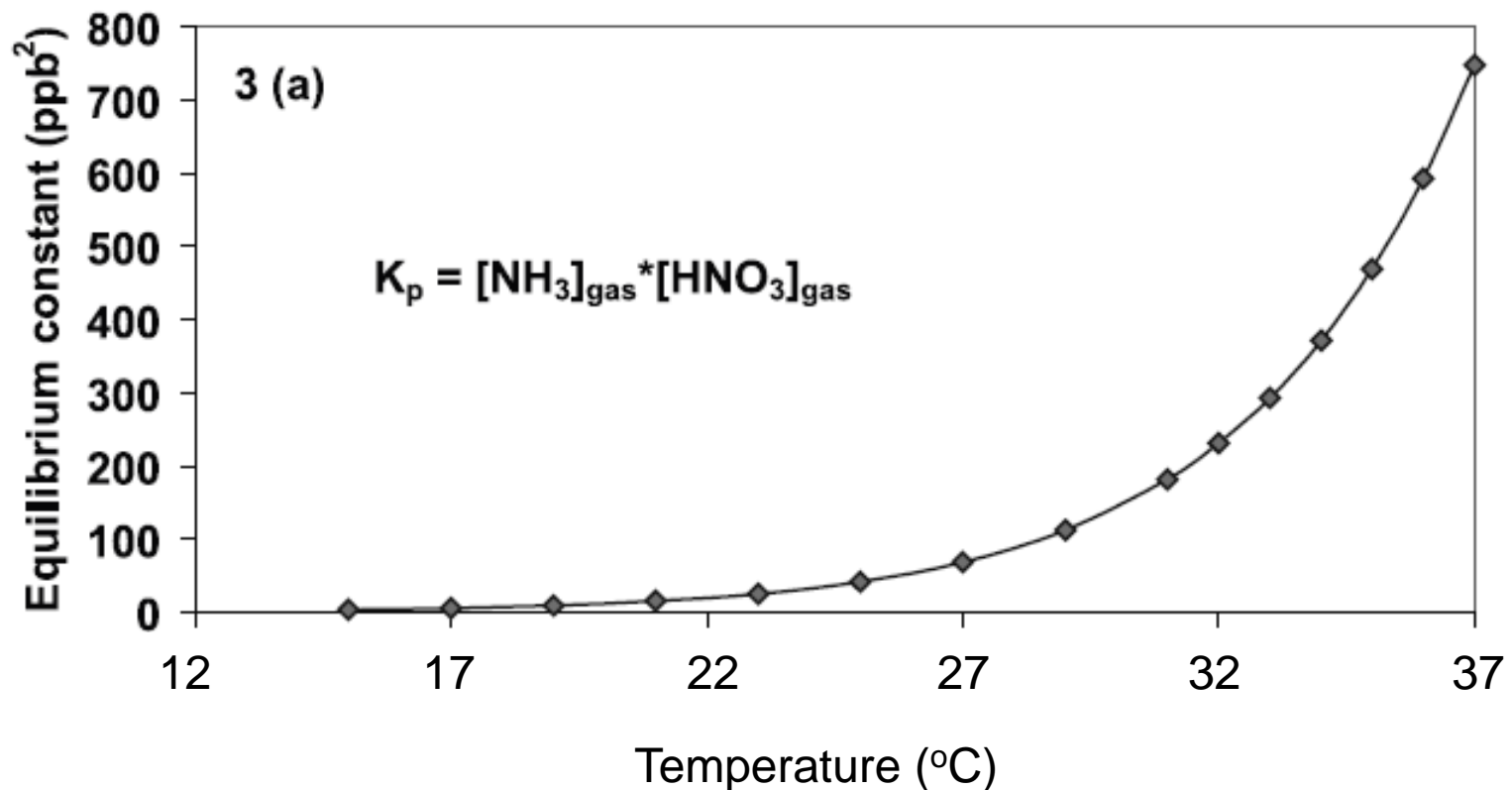
Nighttime/Winter Nitrate Formation



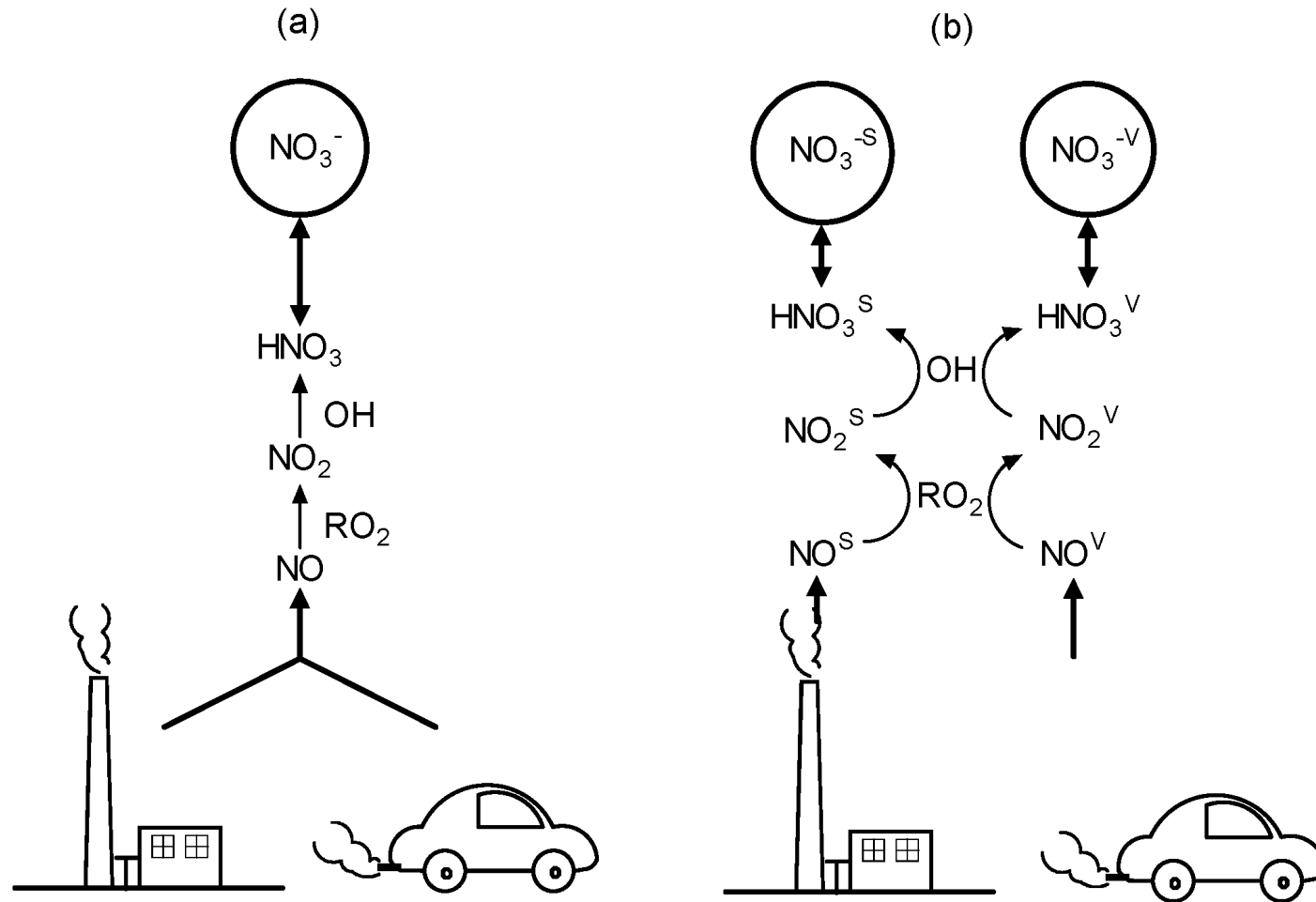
- Main oxidant is O_3 – favors low sunlight intensity, wet conditions

Equilibrium Dissociation Constant for Ammonium Nitrate

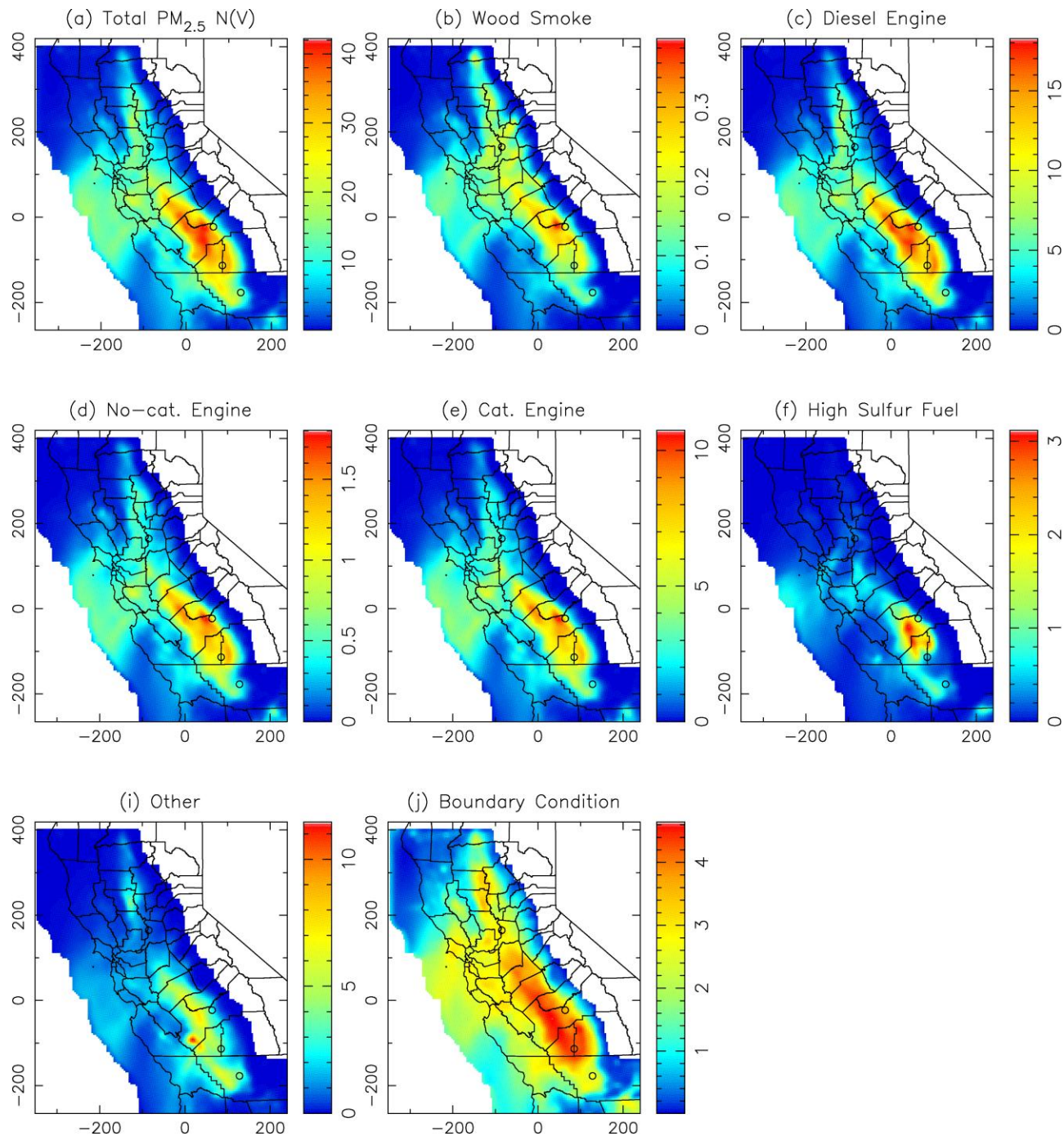
Ammonium nitrate will not form when $[\text{NH}_3][\text{HNO}_3] < K_p$



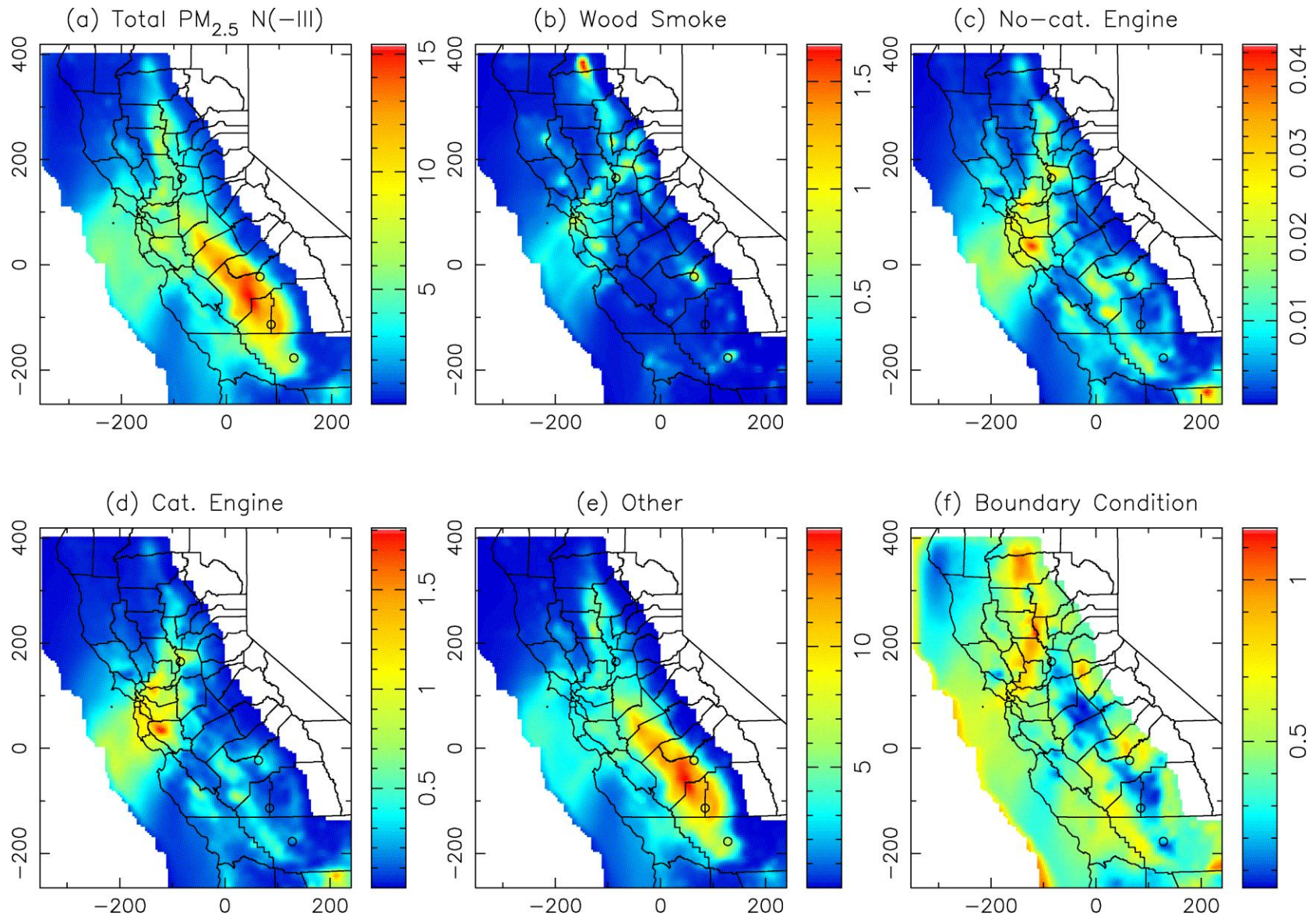
Source Apportionment of Secondary PM



Regional Nitrate Source Contributions

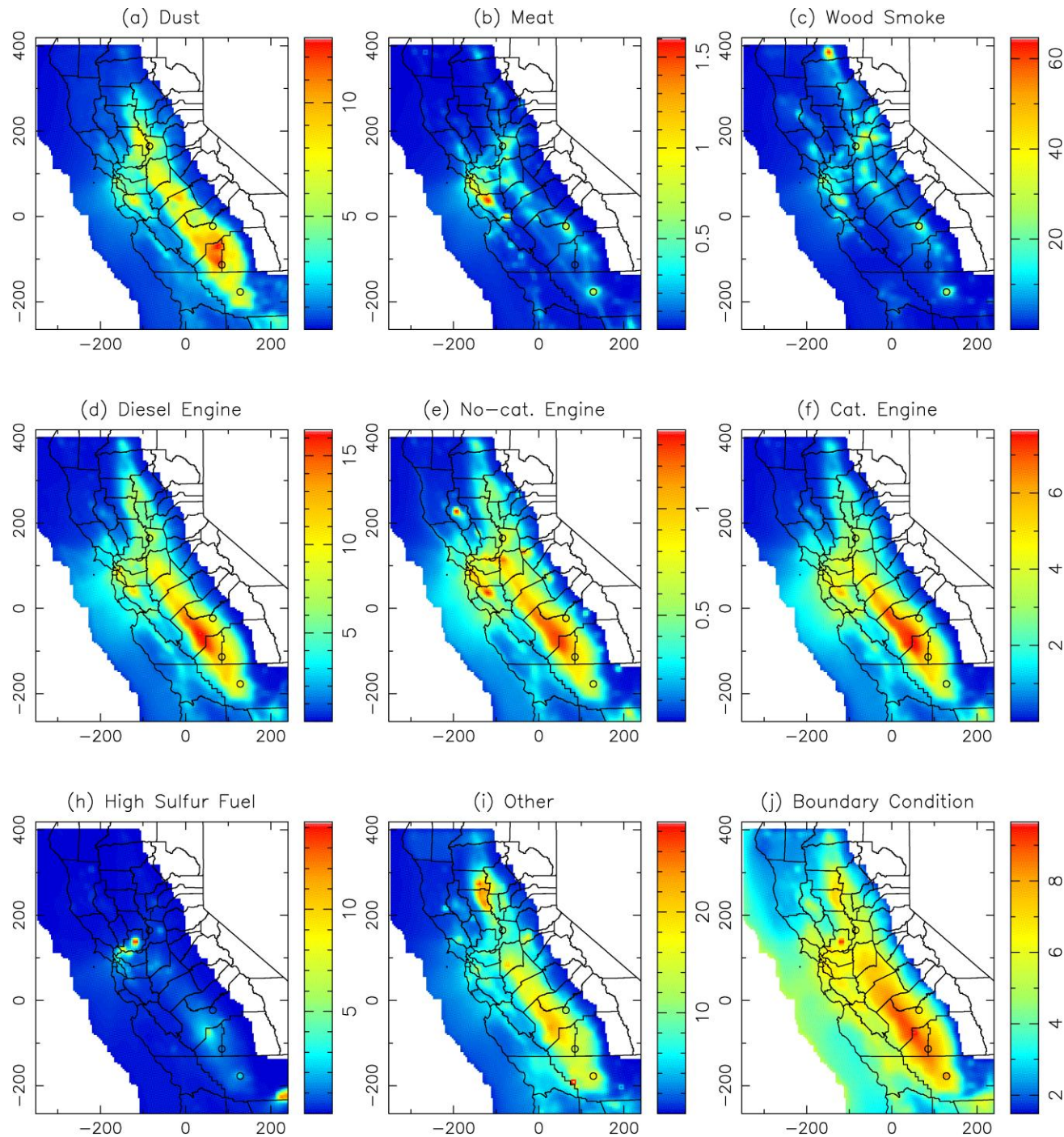


Regional NH₄⁺ Source Contributions



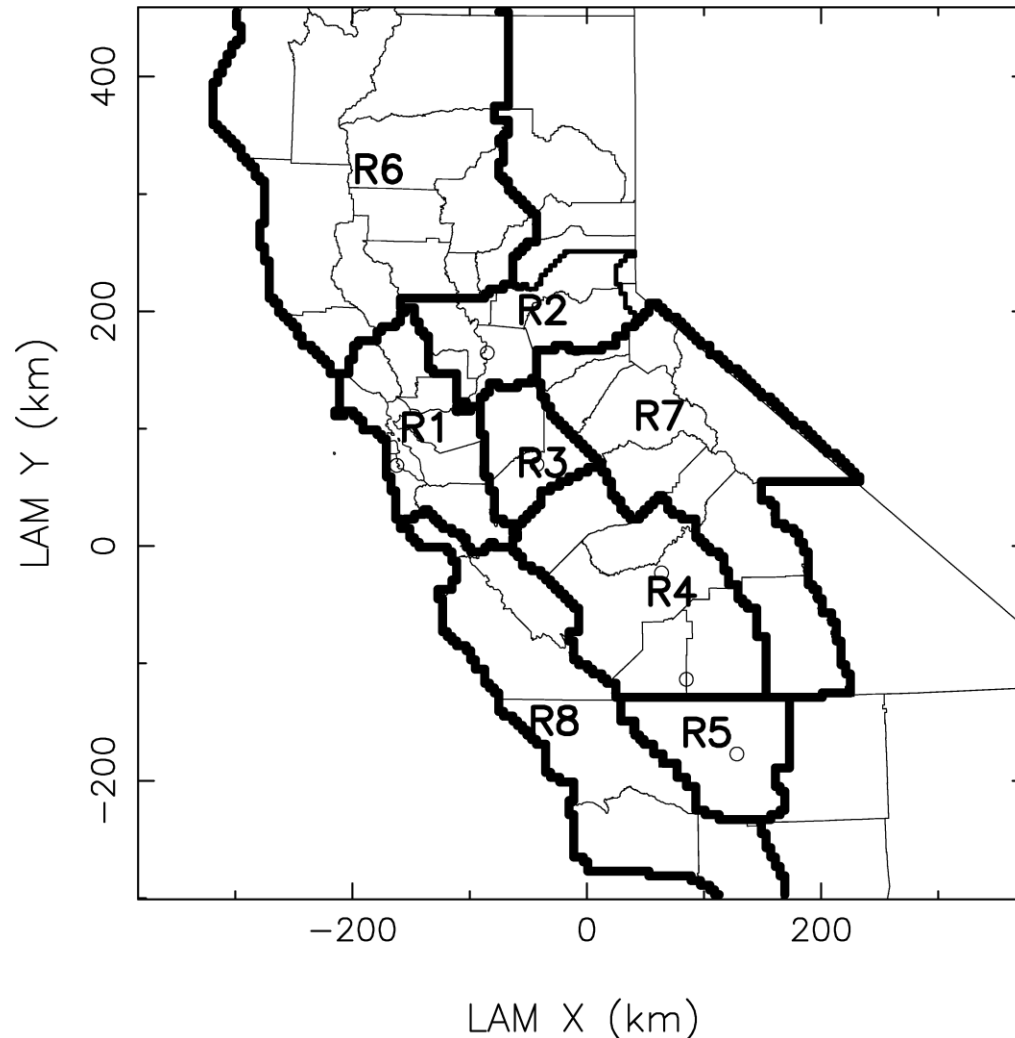
Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part III. Regional Source Apportionment of Secondary and Total Airborne PM_{2.5} and PM_{0.1}.", *Atmos. Env.*, 42, pp8967-8978, 2008.

Regional PM_{2.5} (primary + secondary) Source Contributions

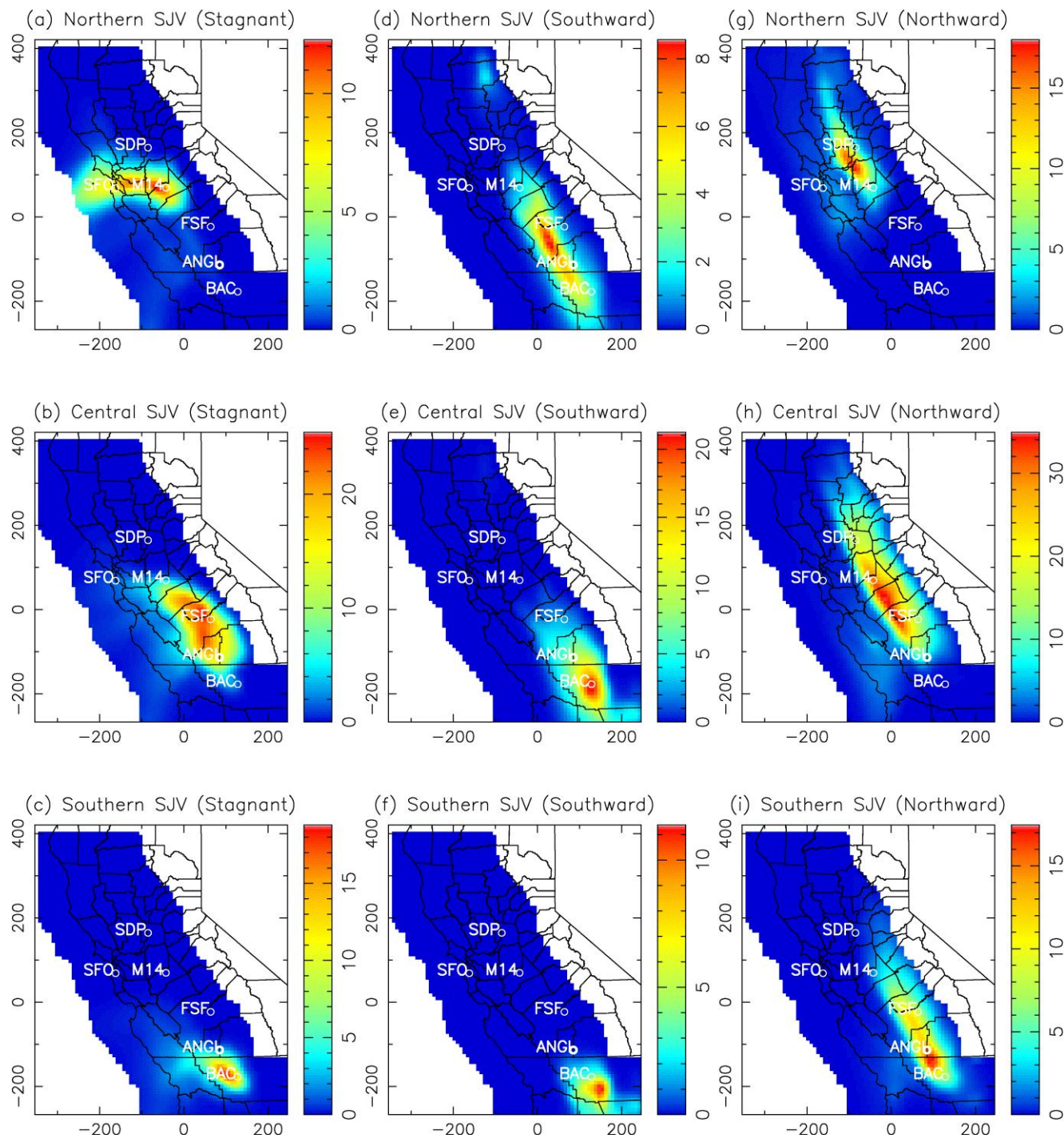


Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part III. Regional Source Apportionment of Secondary and Total Airborne PM_{2.5} and PM_{0.1}.", Atmos. Env., 43, pp419-430, 2009.

How Much PM Does Each Region Contribute to Other Regions?

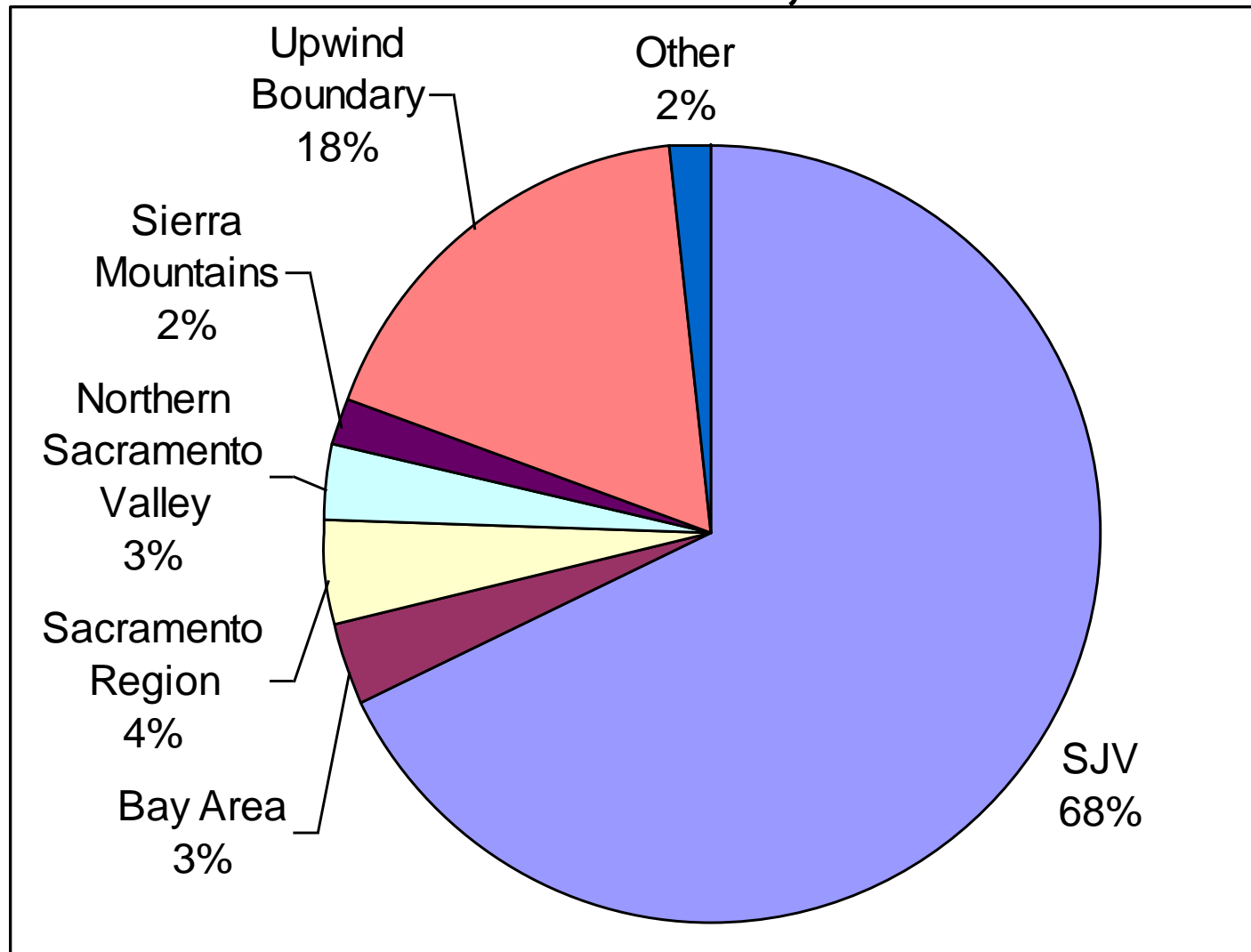


PM_{2.5} Nitrate

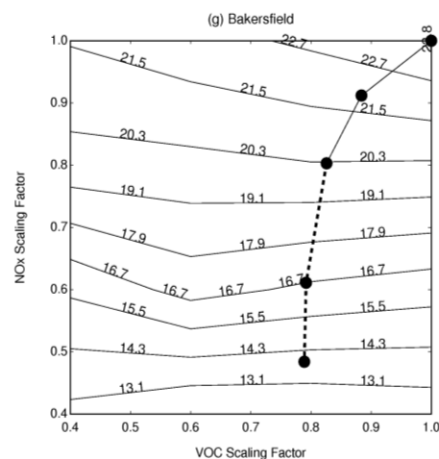
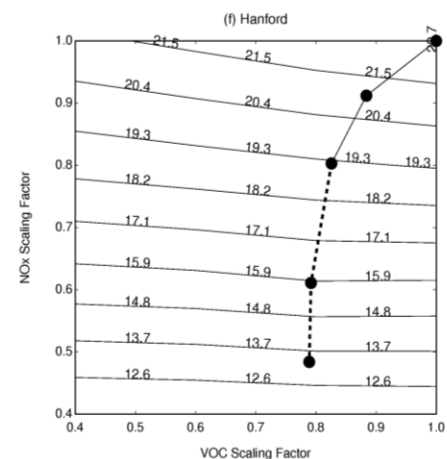
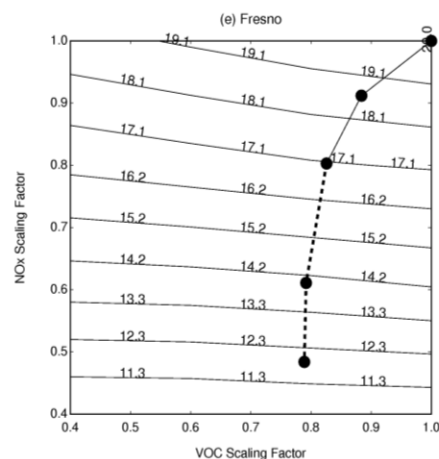
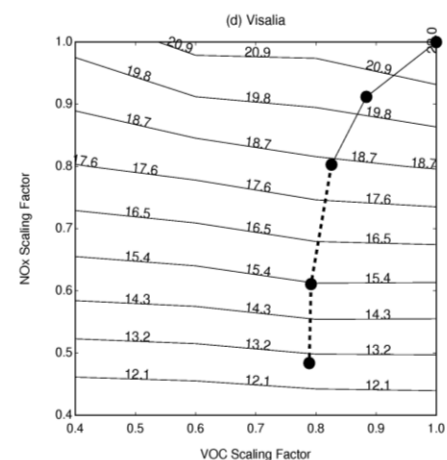
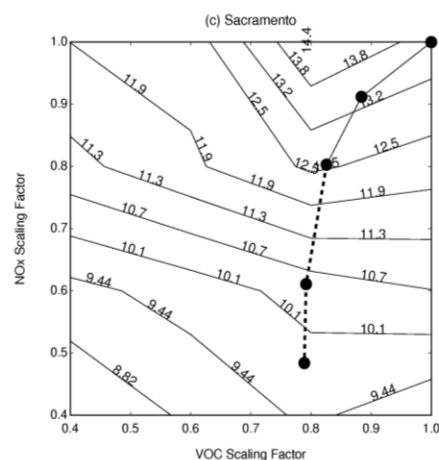


Source: Q. Ying, and M. Kleeman
 "Regional Contributions to Airborne
 Particulate Matter in Central California
 During a Severe Pollution Episode",
 Atmos. Env., 43, 1218-1228, 2009.

Regional Contributions to SJV PM_{2.5} Nitrate Between Dec 15, 2000 – Jan 7, 2001



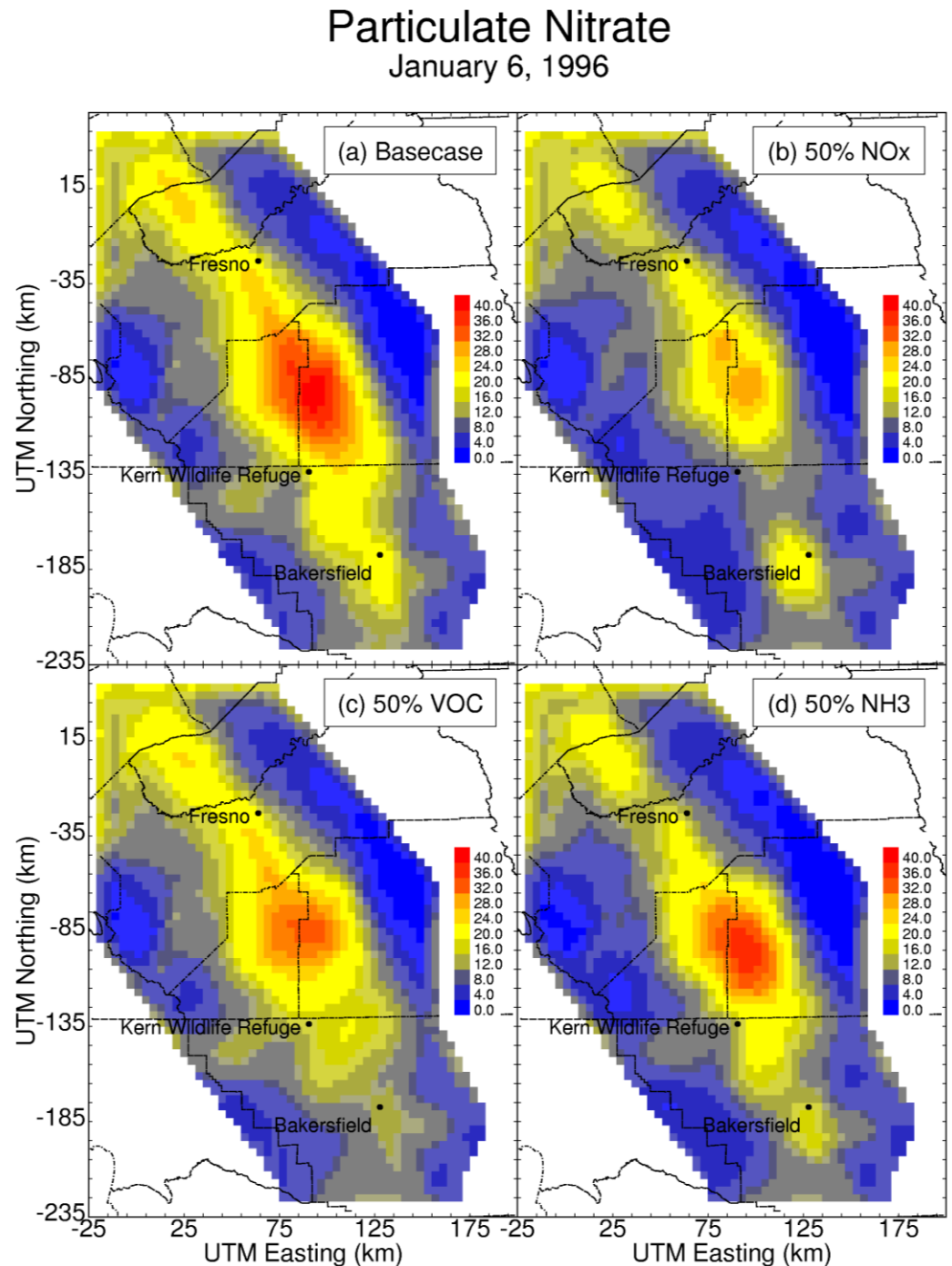
Nitrate Control Options



Maximum 24-hr average PM_{2.5} nitrate concentrations response to NO_x and VOC controls on December 31, 2000 using the SAPRC 90 chemical mechanism. Solid line with dots represents estimated emissions control trajectory since the year 2000 and dashed line with dots represents projected emissions controls through the year 2020 based on the California Almanac for Emissions.

Control Strategy Effectiveness

Source: Kleeman MJ, Ying Q, Kaduwela A. Control strategies for the reduction of airborne particulate nitrate in California's San Joaquin Valley. Atmospheric Environment 39: 5325-5341, 2005.



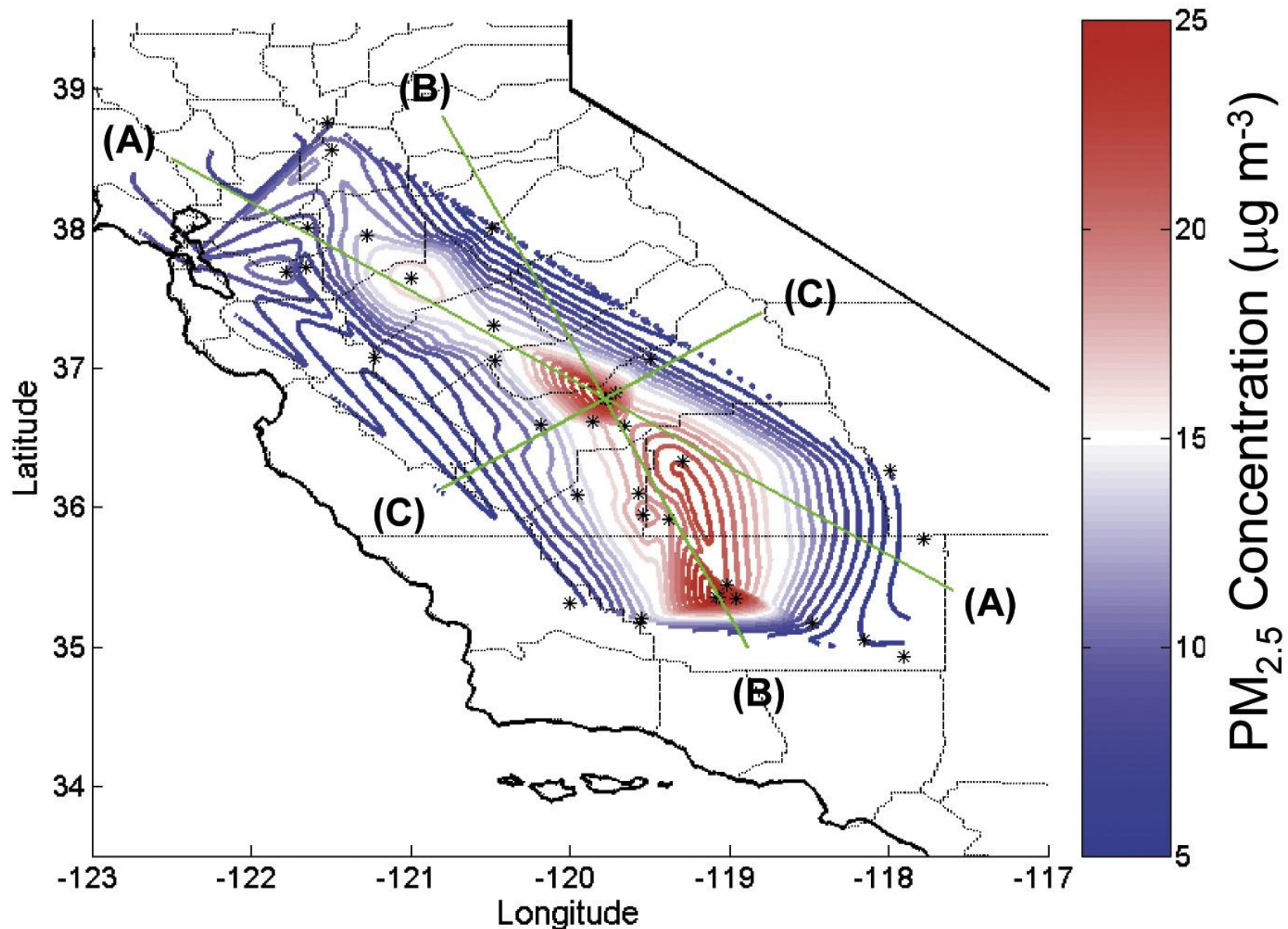
Research vs. Regulatory Models

- Research Model
 - Develop new techniques
 - Emphasis on science
 - Usually increased costs
- Regulatory Model
 - Accepted techniques
 - Emphasis on practicality



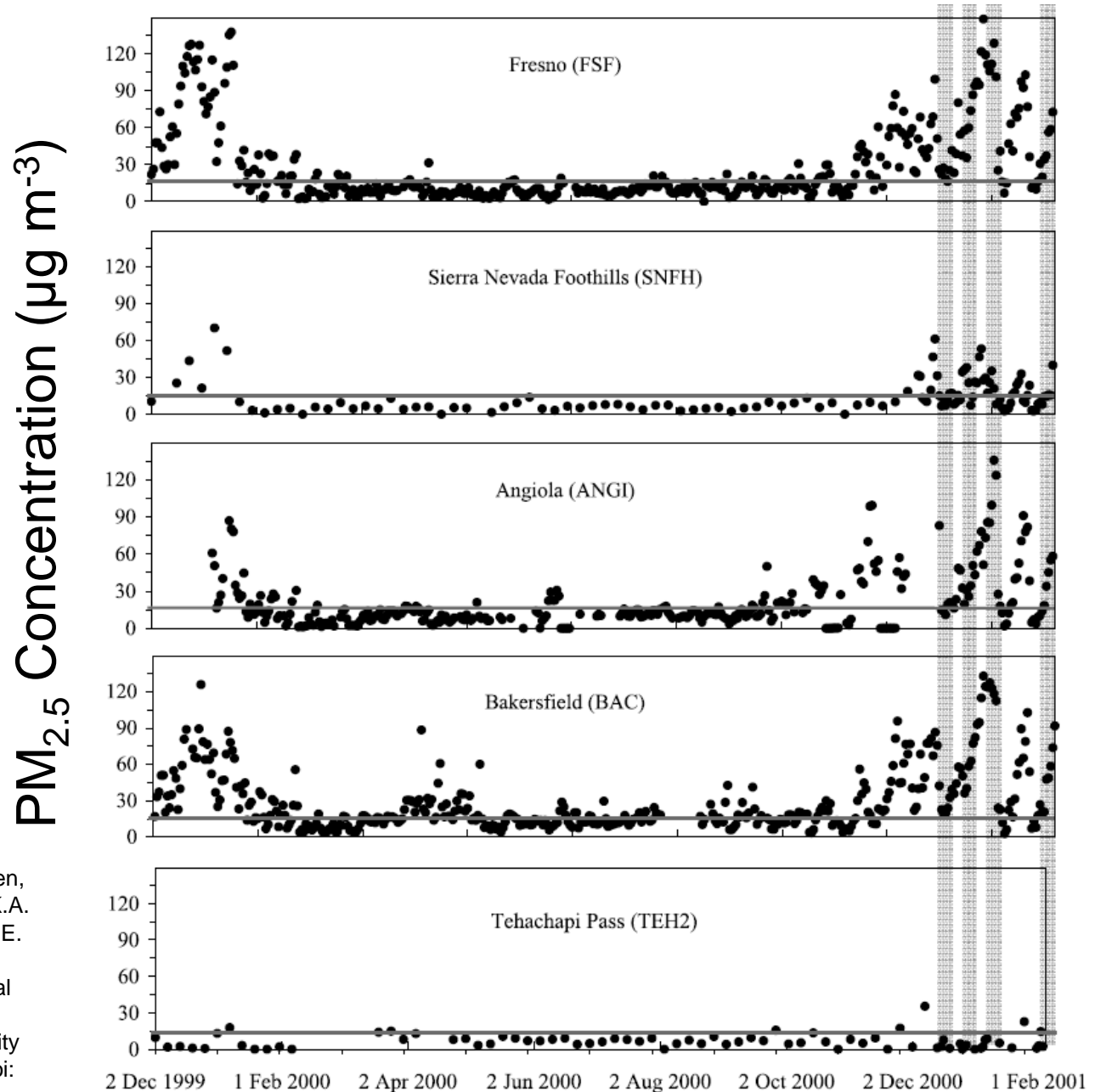
EXTRA SLIDES

PM_{2.5} Concentrations in the SJV



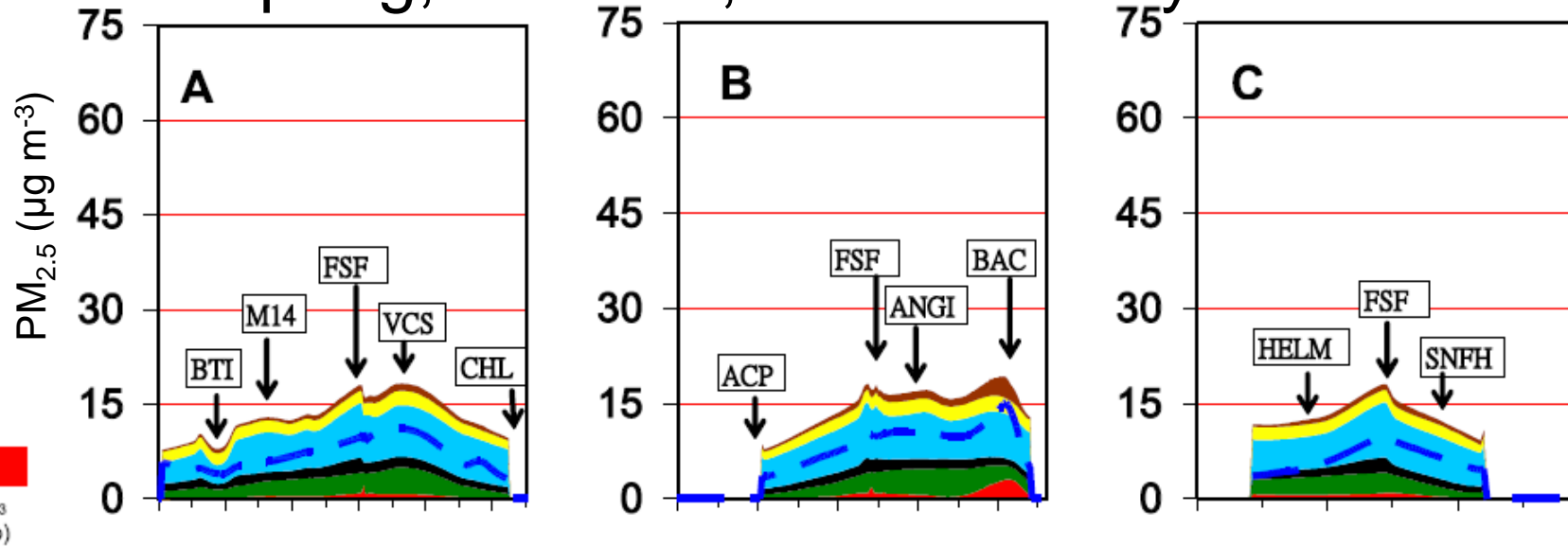
Feb 1, 2000 – Jan 31, 2001

PM_{2.5} Seasonal Variation in the SJV

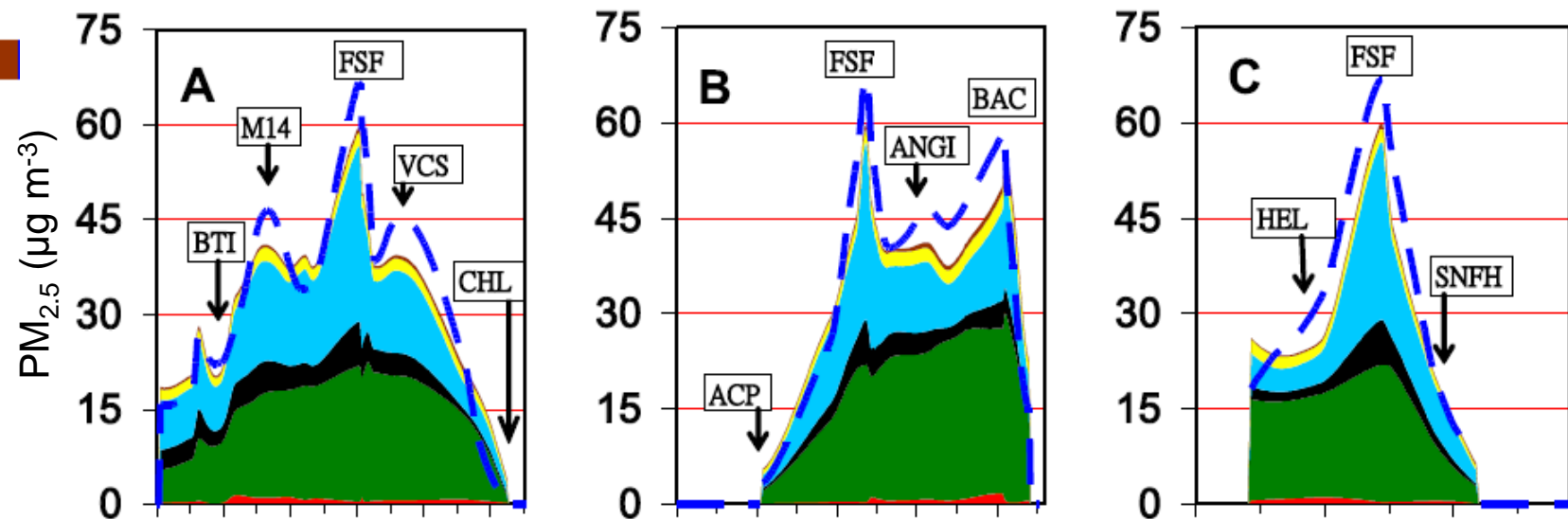


Source: J.C. Chow, L.W. A. Chen, J.G. Watson, D.H. Lowenthal, K.A. Magliano, K. Turkiewicz, and D.E. Lehrman, "PM_{2.5} Chemical Composition and Spatiotemporal Variability During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS), JGR, 111, doi: 10.1029/2005JD006457, 2006.

Spring, Summer, Fall: February - October



Winter: November - January

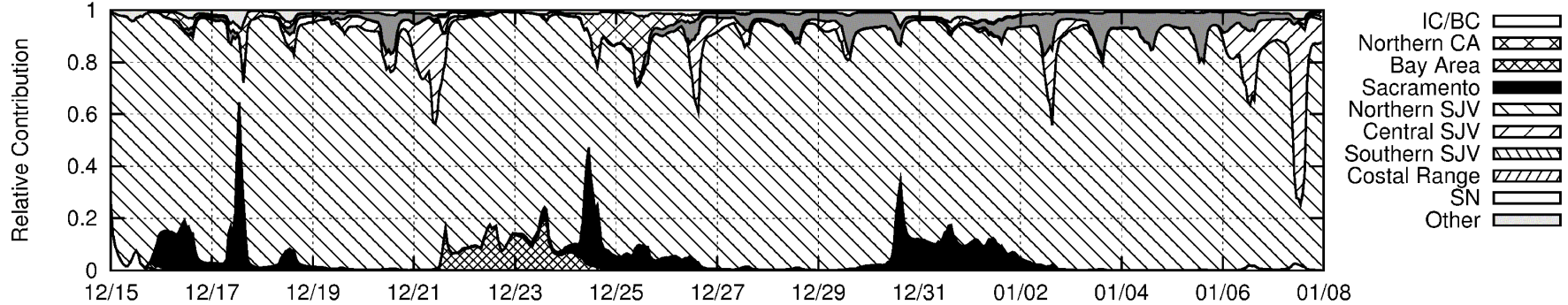


Daytime/Summer Nitrate Formation

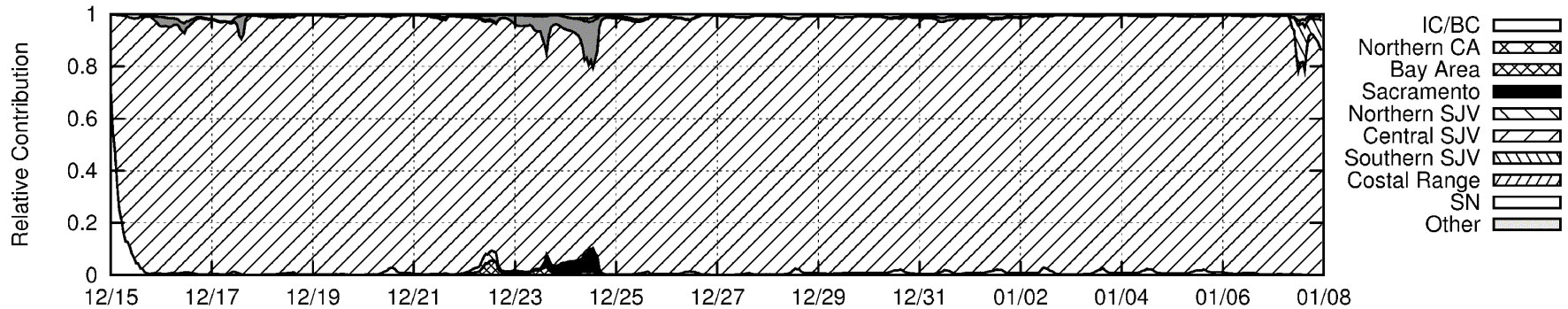
- $\text{NO} \xrightarrow{\text{O}_3} \text{NO}_2 \xrightarrow{\text{OH}} \text{HNO}_3$
- Main oxidant is OH – requires high sunlight, VOC rich environment

OC Region Contributions

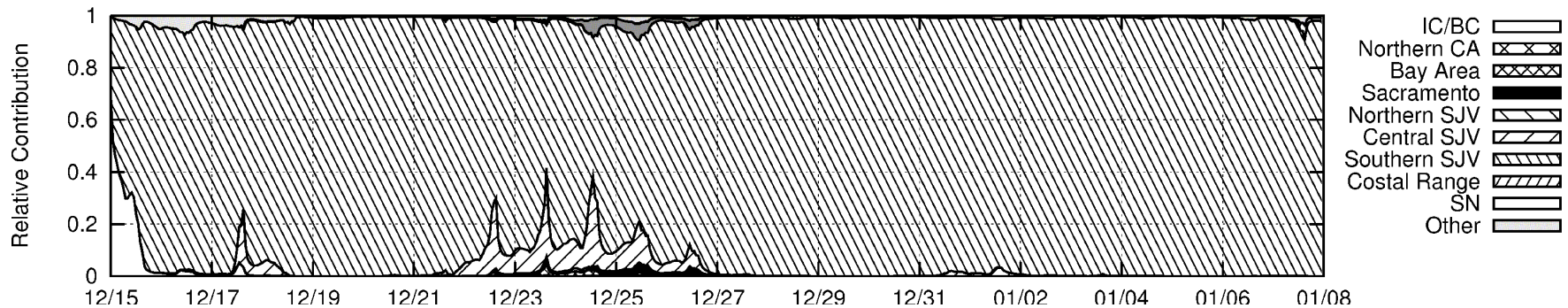
(a) Modesto



(b) Fresno

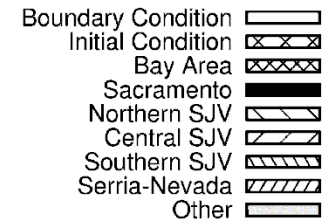
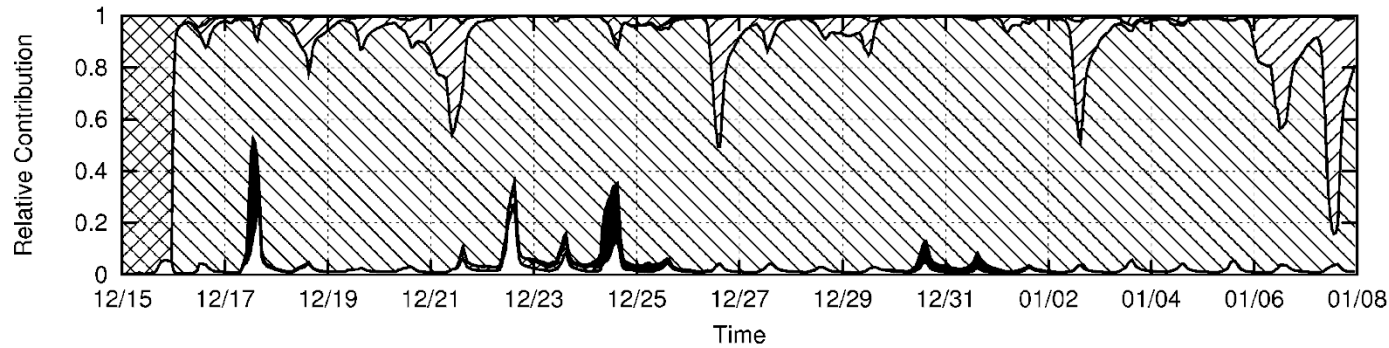


(e) BAC

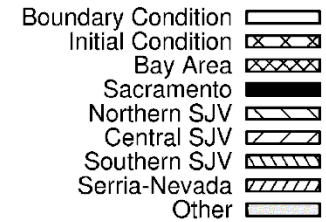
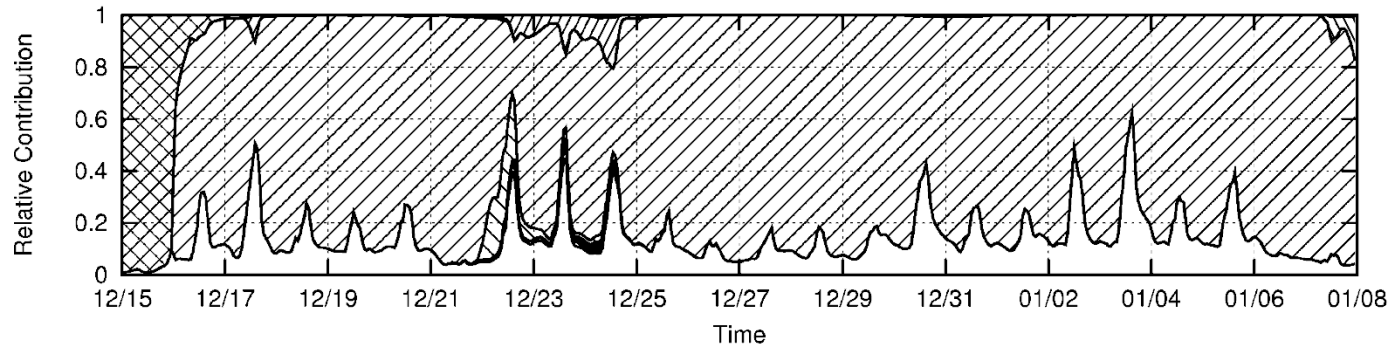


Ammonium Region Contributions

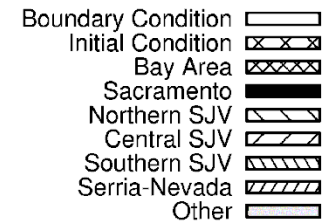
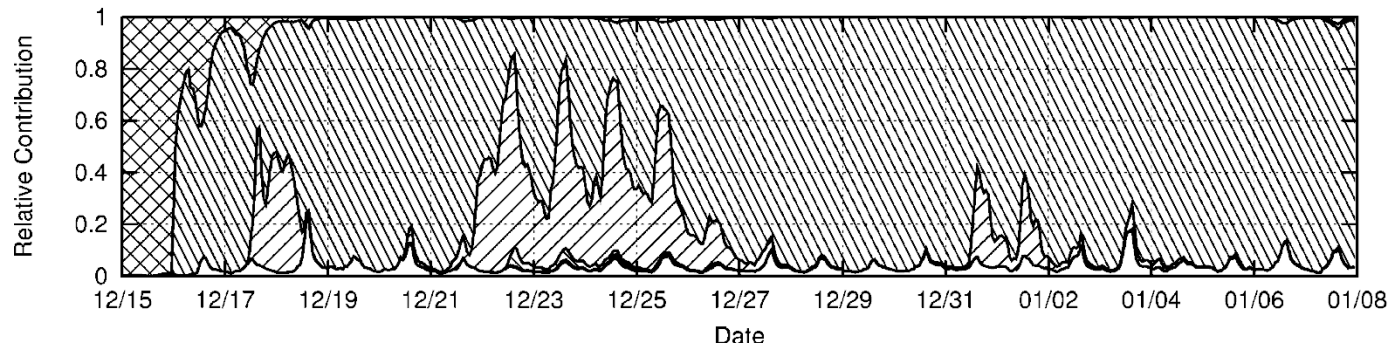
(a) Modesto



(b) Fresno

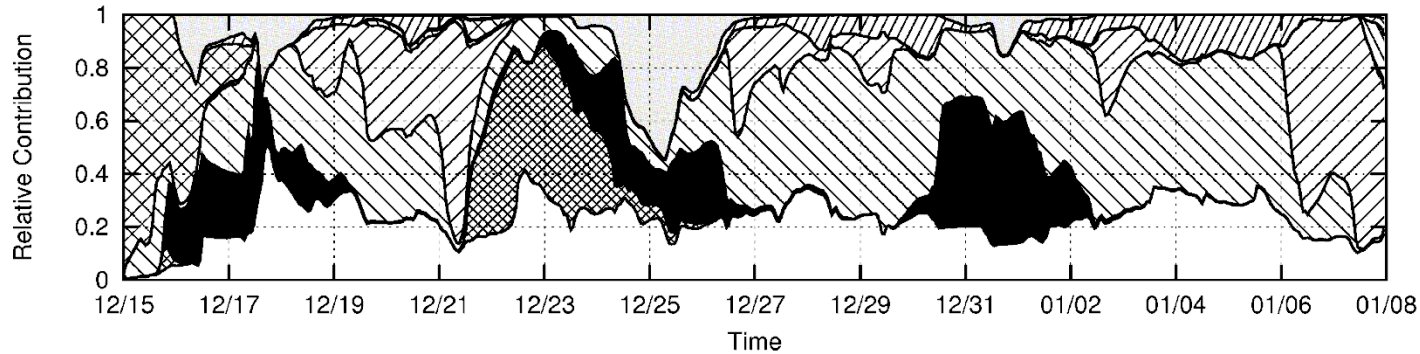


(c) Bakersfield

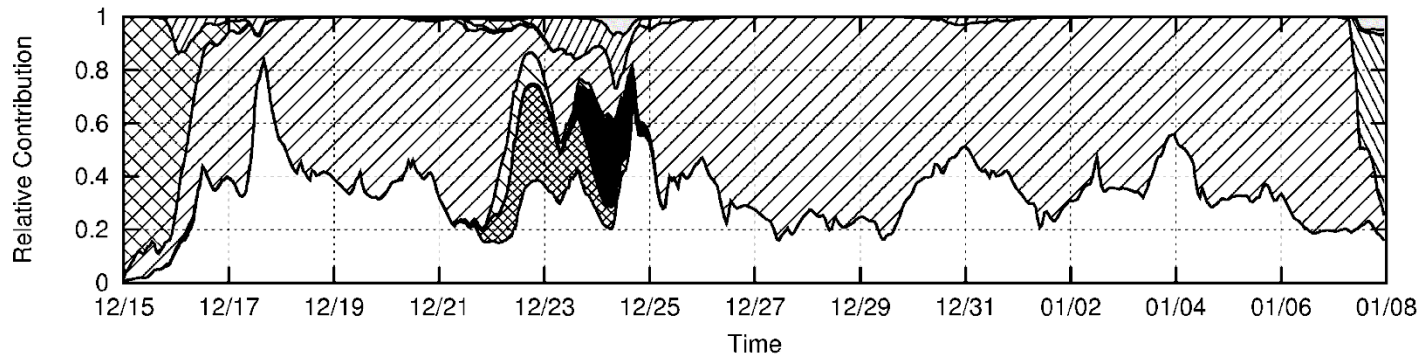


Nitrate Region Contributions

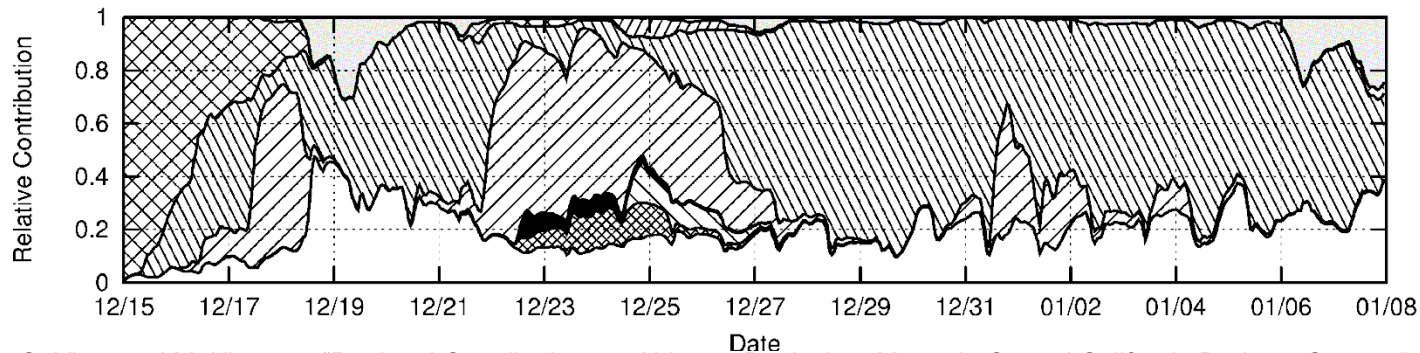
(a) Modesto



(b) Fresno



(c) Bakersfield

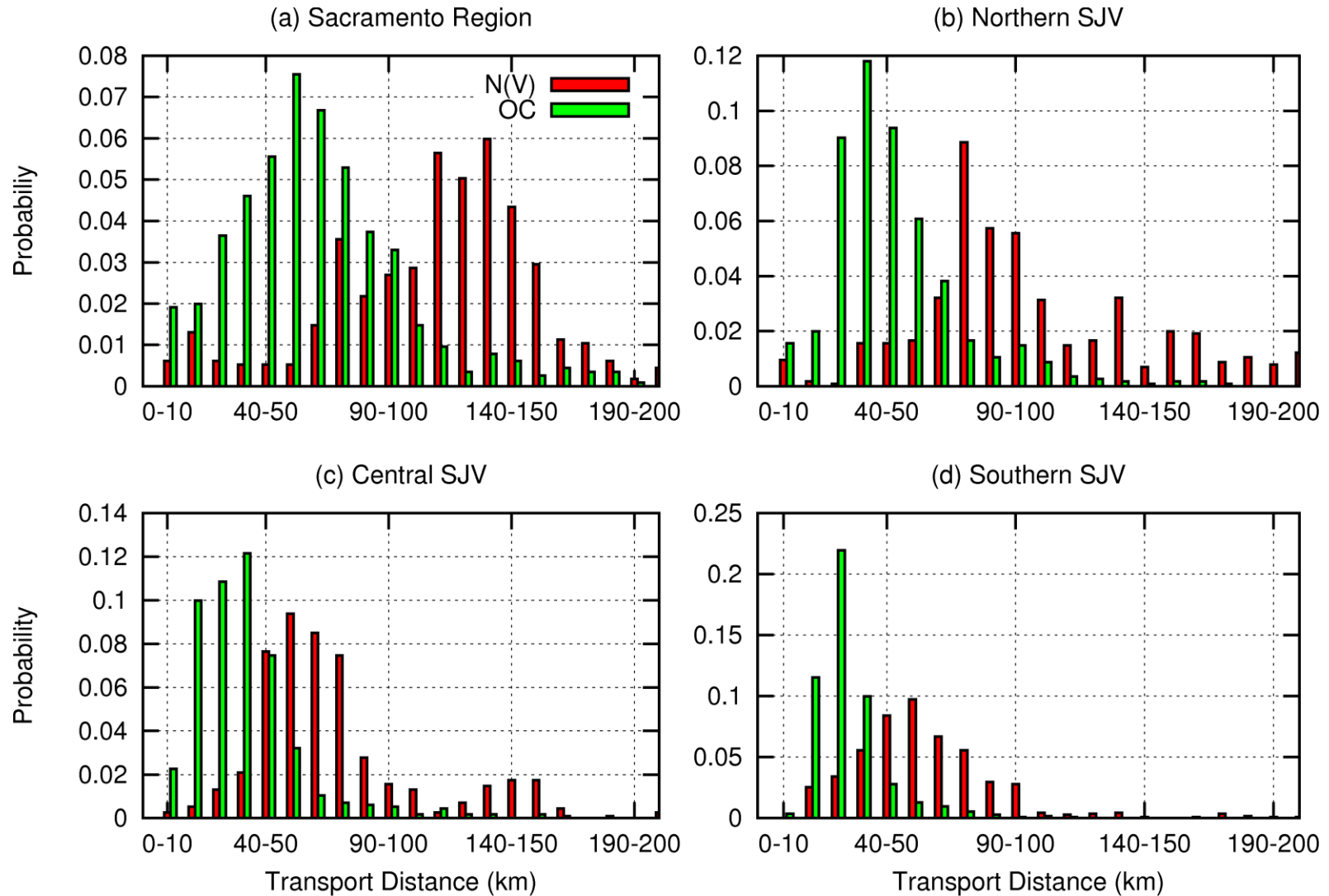


Boundary Condition
Initial Condition
Bay Area
Sacramento
Northern SJV
Central SJV
Southern SJV
Serria-Nevada
Other

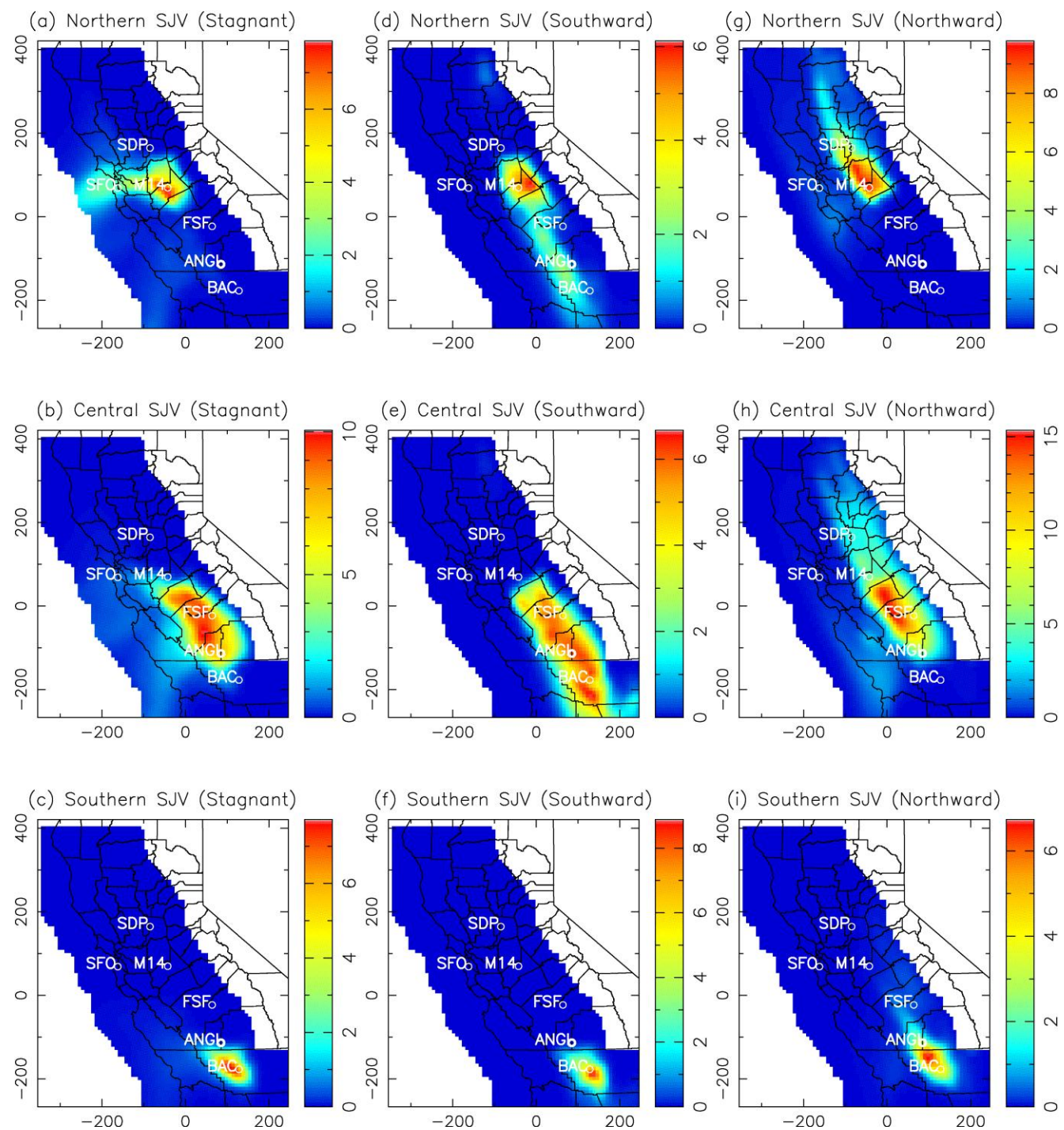
Boundary Condition
Initial Condition
Bay Area
Sacramento
Northern SJV
Central SJV
Southern SJV
Serria-Nevada
Other

Boundary Condition
Initial Condition
Bay Area
Northern SJV
Sacramento
Central SJV
Southern SJV
Serria-Nevada
Other

Distribution of Transport Distances



PM_{2.5} Ammonium



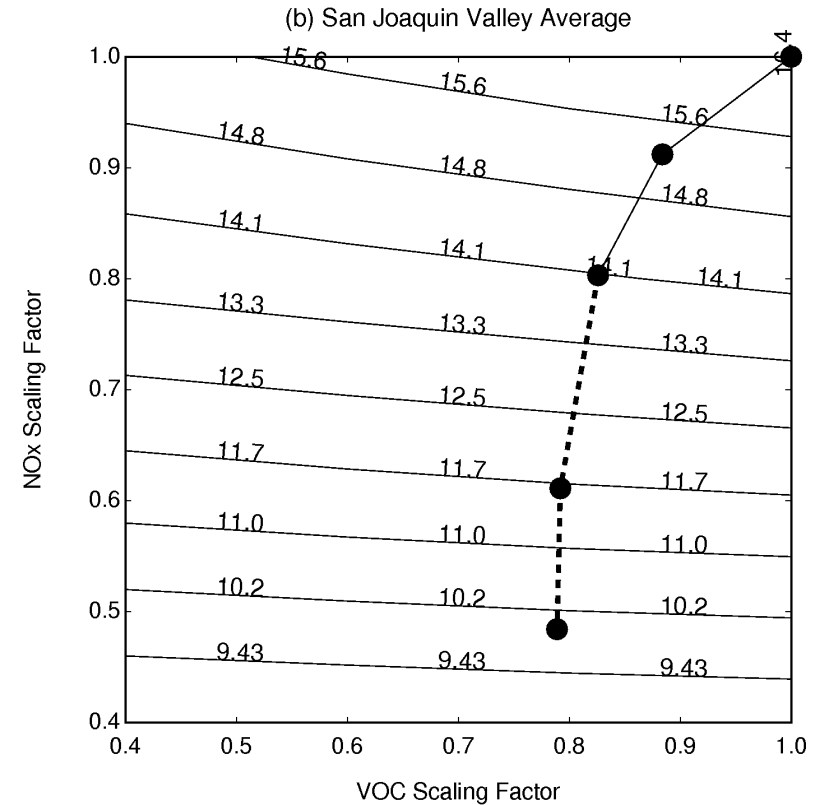
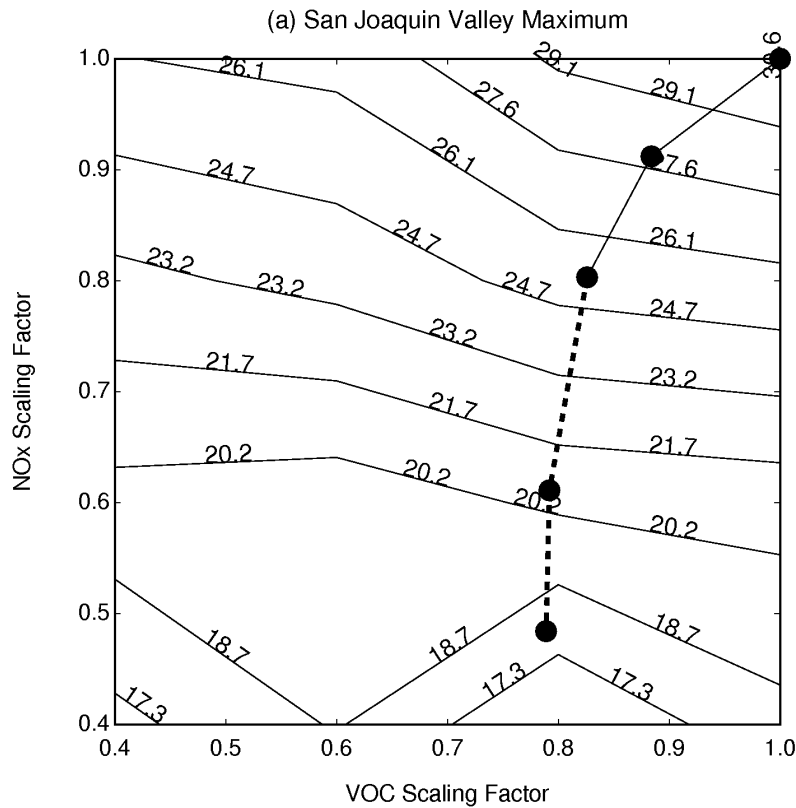
Source: Q. Ying, and M. Kleeman
 “Regional Contributions to Airborne
 Particulate Matter in Central California
 During a Severe Pollution Episode”,
 Atmos. Env., 43, 1218-1228, 2009.

Nitrate Regional Contribution Summary

Source Receptor		BC	Bay Area	Sac	N SJV	C SJV	S SJV	N SacV	Sierra	Other	
		S0	S1	S2	S3	S4	S5	S6	S7	S8	SUM
Bay Area	R1	2.1%	1.5%	1.8%	1.4%	0.4%	0.0%	0.2%	0.2%	0.7%	8.2%
Sac	R2	1.1%	0.2%	1.3%	0.3%	0.3%	0.0%	0.1%	0.1%	0.8%	4.3%
N SJV	R3	1.3%	0.3%	0.8%	1.7%	1.0%	0.0%	0.1%	0.4%	0.2%	5.9%
C SJV	R4	5.0%	0.8%	0.9%	1.7%	17.7%	0.7%	0.8%	0.4%	0.3%	28.3%
S SJV	R5	1.4%	0.3%	0.2%	0.2%	3.1%	3.1%	0.4%	0.0%	0.2%	9.0%
N SacV	R6	3.4%	1.1%	0.6%	1.1%	4.0%	1.4%	2.0%	0.1%	0.7%	14.5%
Sierra	R7	0.5%	0.1%	0.1%	0.1%	0.3%	0.0%	0.1%	0.2%	0.0%	1.5%
Other	R8	8.4%	3.9%	2.3%	1.7%	2.4%	0.6%	2.3%	0.2%	6.5%	28.4%
SUM		23.2%	8.2%	8.1%	8.2%	29.3%	6.0%	6.0%	1.6%	9.4%	100.0%

Source: Q. Ying, and M. Kleeman “Regional Contributions to Airborne Particulate Matter in Central California During a Severe Pollution Episode”, Atmos. Env., 43, 1218-1228, 2009.

Nitrate Control Options



Maximum 24-hr average PM_{2.5} nitrate concentrations response to NO_x and VOC controls on December 31, 2000 using the SAPRC 90 chemical mechanism. Solid line with dots represents estimated emissions control trajectory since the year 2000 and dashed line with dots represents projected emissions controls through the year 2020 based on the California Almanac for Emissions.

Partial Answers

- *Primary vs. secondary PM 2.5 species*
 - *Elemental carbon (EC), organic carbon (OC), ammonium nitrate*
- *Sources of PM 2.5 in the region?*
 - *Wood smoke (OC) and diesel engines (EC) in urban areas*
 - *Diesel engines (nitrate) and gasoline engines (nitrate) contribute regionally*
 - *Agricultural activities (ammonium) contribute regionally*

Partial Answers

- *Why do they concentrate in winter?*
 - *Lower mixing depths, colder temperature, home heating*
- *Where and when do PM 2.5 concentrations vary in the Valley?*
 - *Transport can be a factor, but mostly local emissions cause local air pollution*
- *What types of control measures have been most successful?*
 - *Restrictions on residential wood combustion*
 - *Restrictions on NO emissions*

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